Nanopores, Nanoparticles, and "Molecular Hydrides" for Hydrogen Production, Transport, and Storage Production, Transport, and Storage of Fuels

SAND2019-13807PE

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HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

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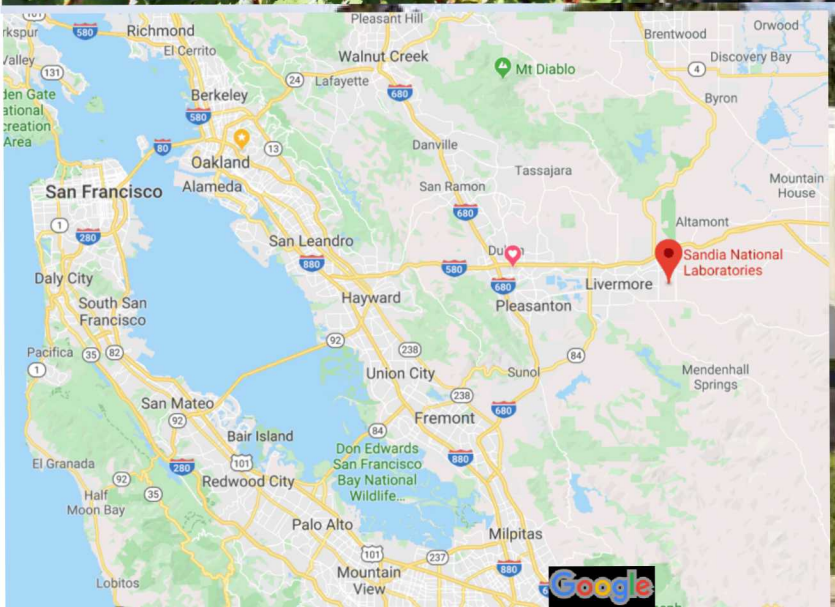
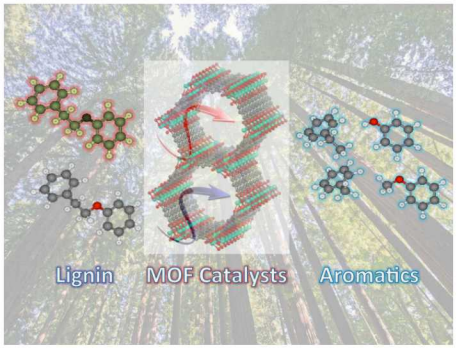
Sandia's California site is in the San Francisco Bay Area

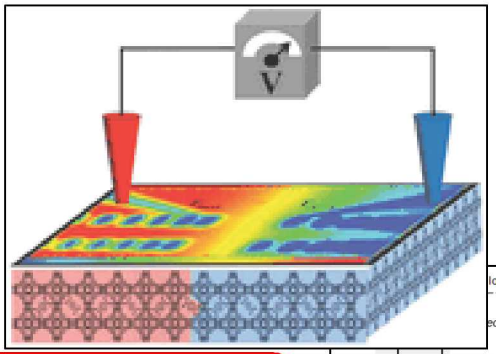


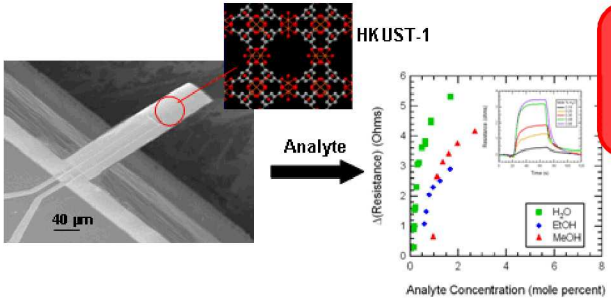
Materials chemistry and device research at Sandia-California using Metal-Organic Frameworks (MOFs)

Hydrogen storage

Catalysts for biomass upgrading



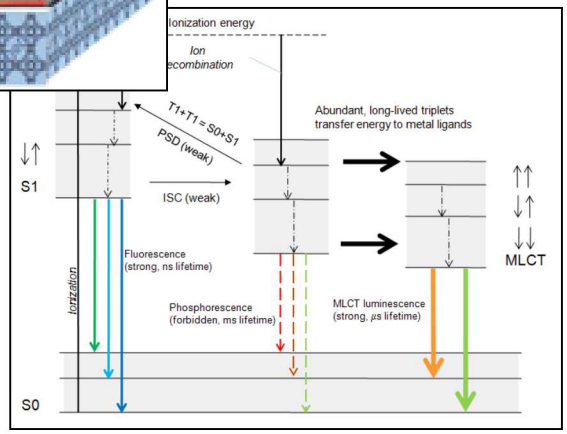




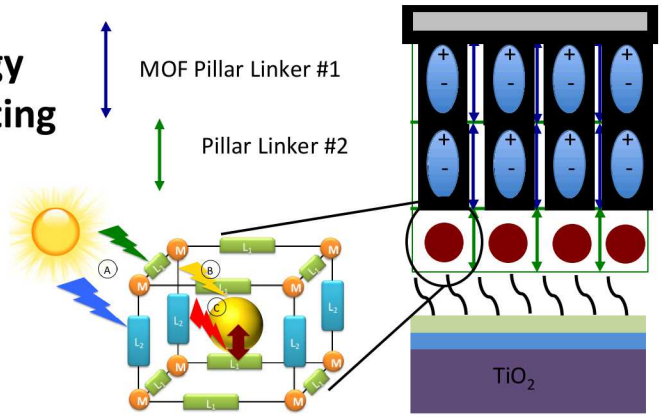
Chemical sensing

Hybrid/nanoscale conducting materials

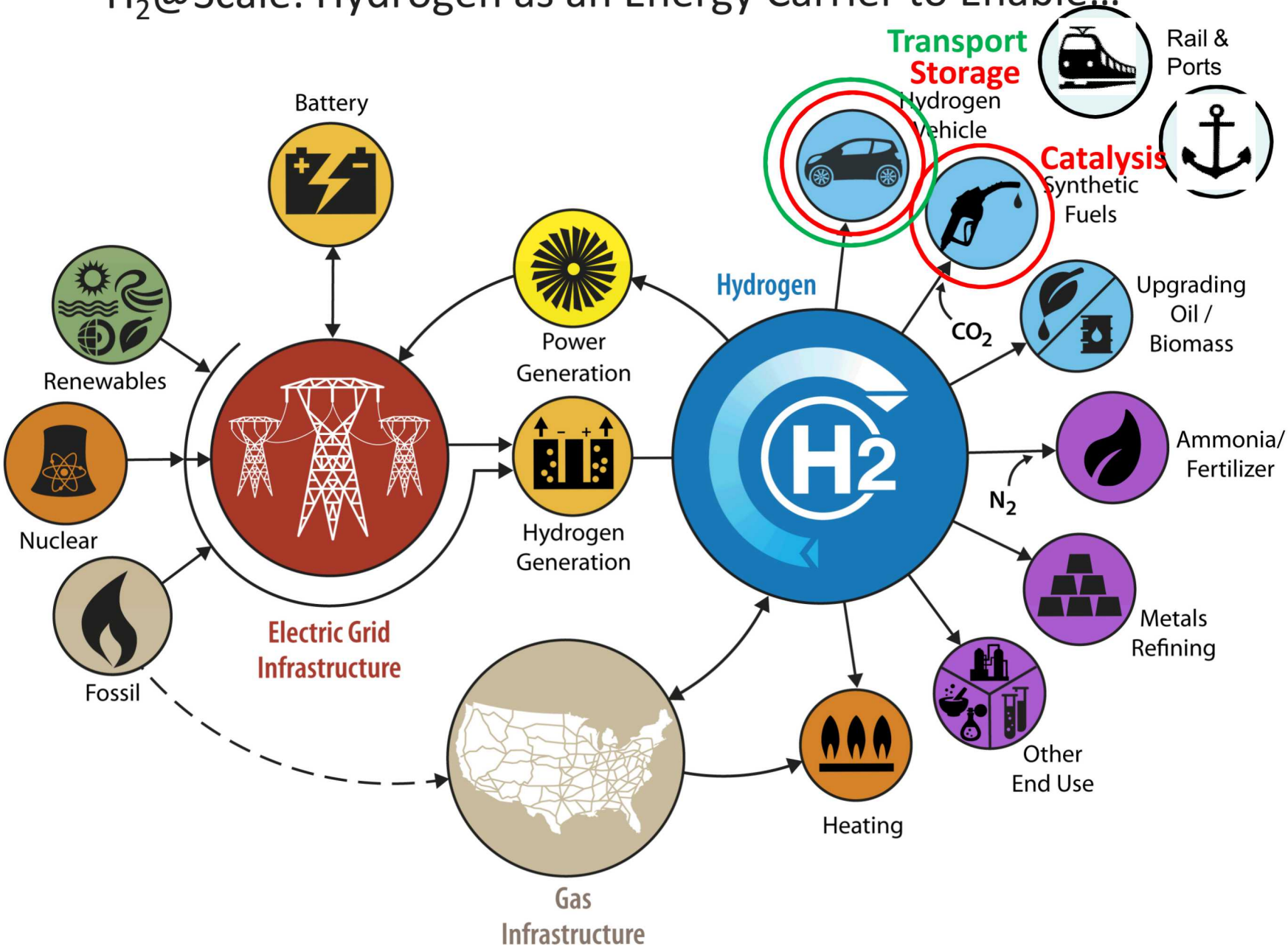
Light emission/radiation detection



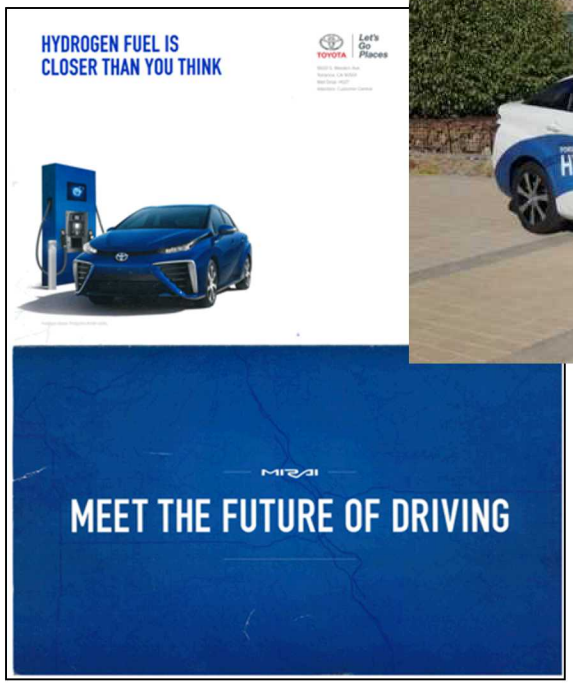
Energy harvesting



H_2@Scale: Hydrogen as an Energy Carrier to Enable…

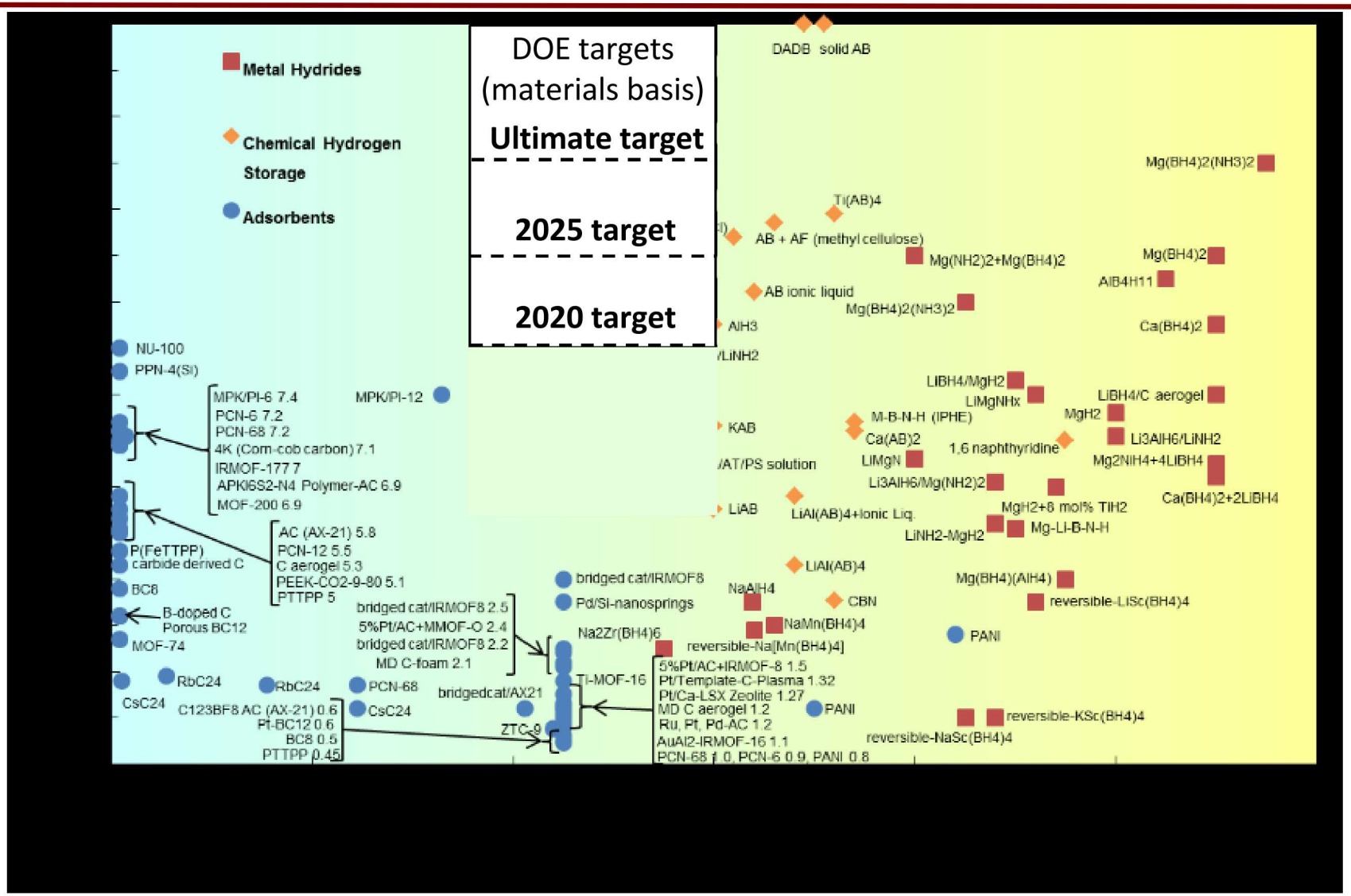


Hydrogen-powered cars are now commercially available



- 700 bar pressurized tanks
- 265 – 312 mile range
- Refueling stations being installed in some areas

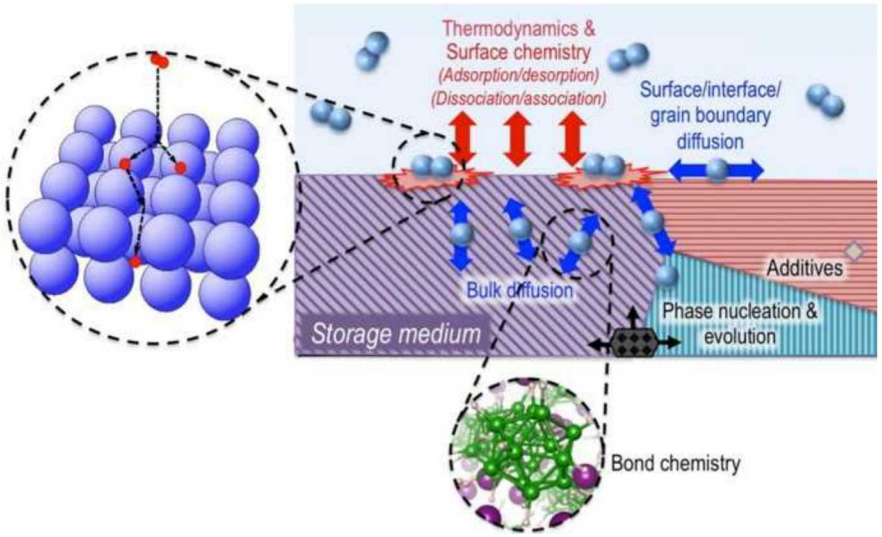
2005-2013: 3 DOE/EERE-funded Centers of Excellence focused on materials development



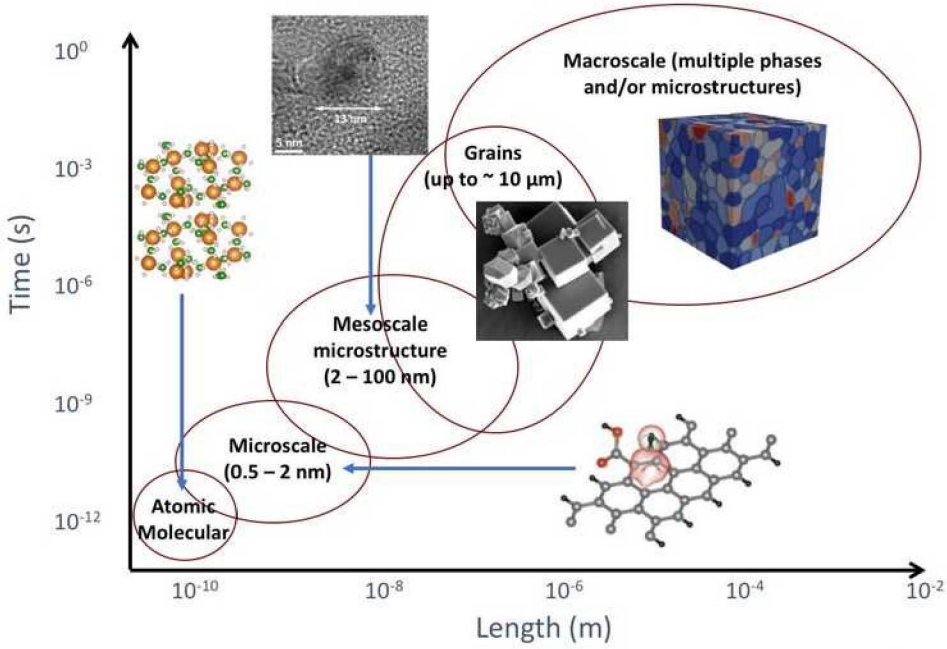
Although many materials were investigated, none were identified that met all DOE technical targets

Poorly understood phenomena at length scales from < 1 nm to μm govern storage material behavior

Distinct chemical/physical processes affect the bulk properties of storage materials



Multiple length scales must be taken into account



"Design rules" are needed to guide materials discovery

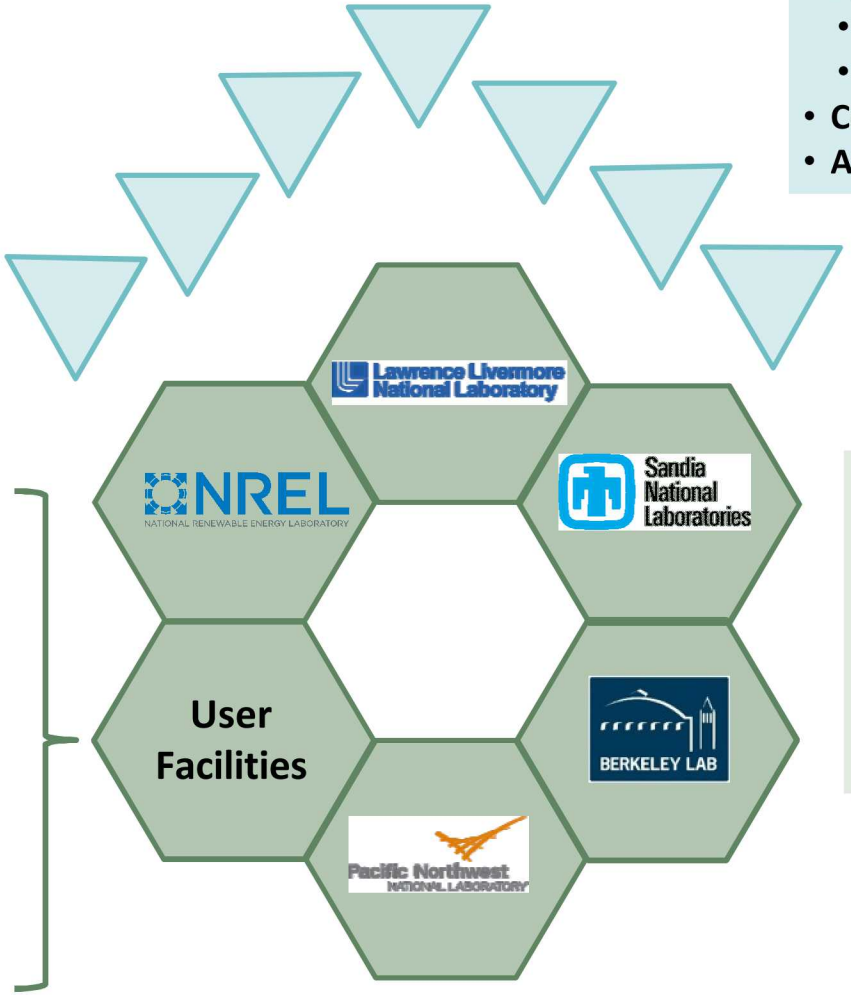
Hydrogen Materials Advanced Research Consortium (HyMARC): highly coordinated capabilities to accelerate materials discovery

HyMARC Phase 1:
- ***FY16 – FY 18***
- ***3 DOE Labs***
- ***Budget $3M/yr***

HyMARC Phase 2:
- ***FY19 – FY22***
- ***5 DOE Labs***
- ***Budget $8 M/yr***

HyMARC
Hydrogen Materials Advanced Research Consortium

Seedling Projects
- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**



NIST Center for Neutron Research

ALS ADVANCED LIGHT SOURCE

MOLECULAR FOUNDRY

SLAC NATIONAL ACCELERATOR LABORATORY

- **Foundational R&D**
- **Computational models**
- **Synthetic protocols**
- **Advanced characterization tools**
- **Validation of material performance**
- **Guidance to FOA projects**
- **Database development**

https://www.hymarc.org/

Activating hydrogen for storage or reaction: a continuum of length scales, morphologies, and reactivity?

$H_2 \rightleftharpoons H + H \quad \Delta H^\circ(298) = 436$ kJ/mol

Storage by chemical bonding: Increasing reactivity (decreasing Ea) → Physisorption

$NaAlH_4 \rightarrow NaH + Al + 1.5H_2 \quad \Delta H^\circ = 40$ kJ/mol H_2

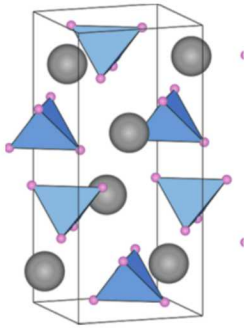
Bulk

2-Steps: $E_a = 118$ kJ/mol H_2
(Incomplete reversibility)
2 mol% Ti: Ea = 80 kJ/mol
(Fully reversible)

Nano

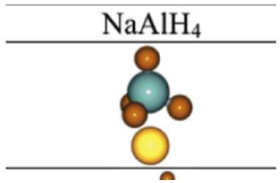
1-Step: $E_a = 58$ kJ/mol
0% Ti: < 2 wt% reversible
3 mol% Ti: 4.1 wt% reversible

$\Delta H^\circ(77K) = 10.7$ kJ/mol

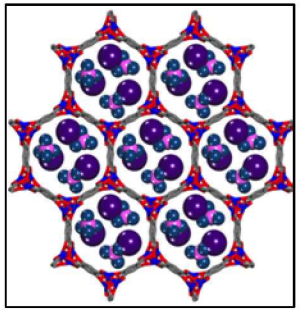


Bulk
Hauback et al.
J. Alloys Compd. 2003, 358, 142

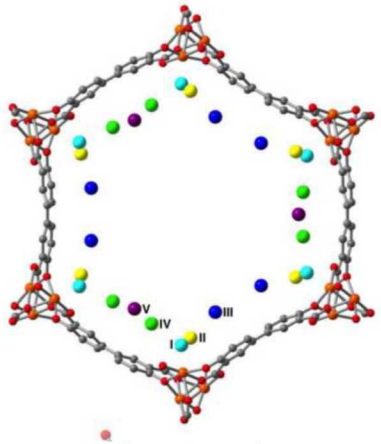
Ball milled



Nanocluster
Mazjoub et al.
JPCC 2011, 115, 2636



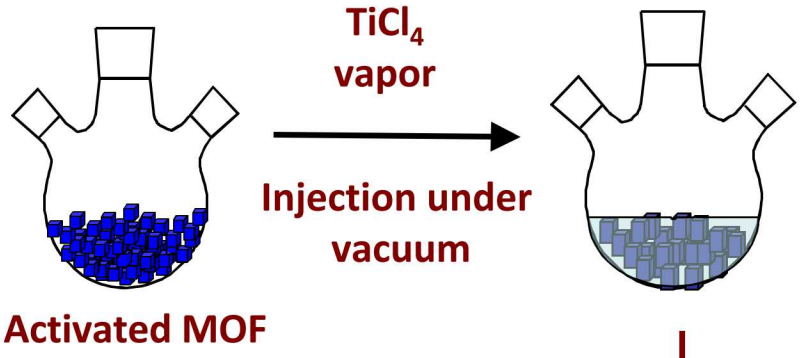
Nanoconfined
Stavila et al.
ACS Nano 2012, 6, 9807

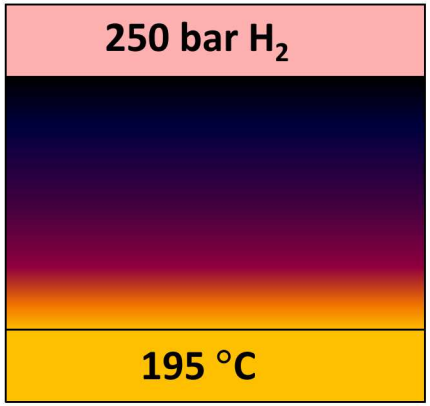


Mg_2(dobdc) MOF
D. Gygi et al.
Chem. Mater. 2016, 28, 1128

MOF-74(Mg) withstands $NaAlH_4$ melt infiltration and doping with Ti catalyst

1) Vapor-phase Ti catalyst infiltration





2) $NaAlH_4$ melt infiltration

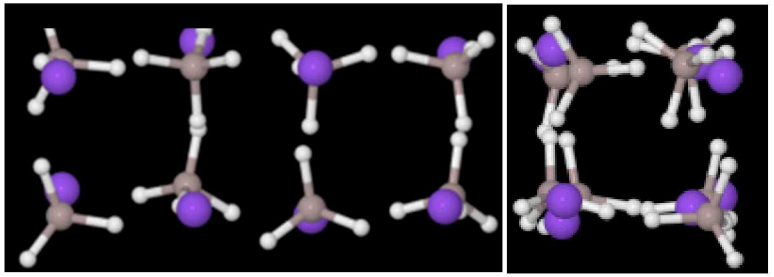
BET surface area:

- **Activated MOF: 1530 m^2/g**
- **Post infiltration → 340 m^2/g**

Loading:

- **~8 formula-unit clusters**
- **Structure optimized by DFT (Prof. Eric Majzoub, UMoStL)**

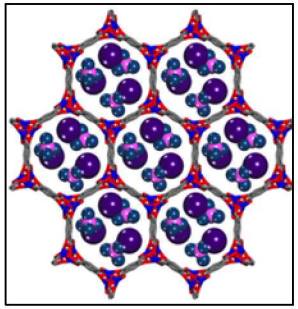
8x8x13 Å



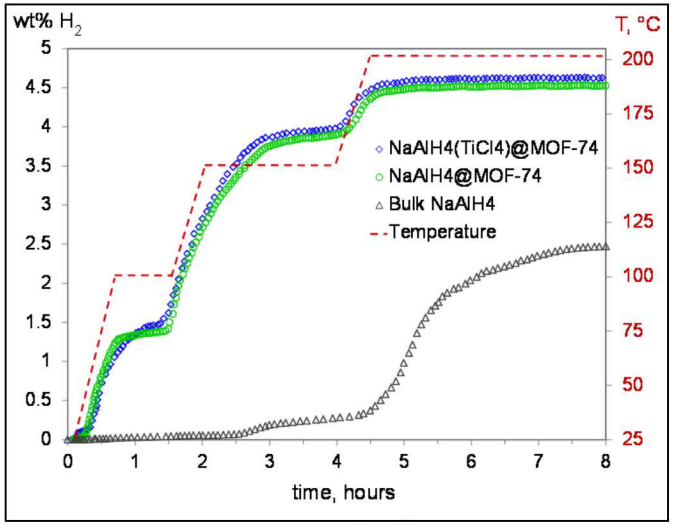
V. Stavila et al. *ACS Nano* 2012, **6**, 9807

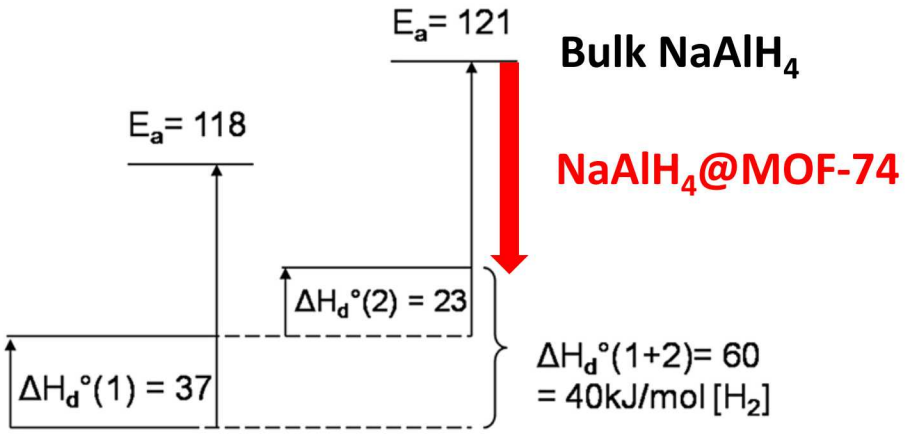
Nanoscaling: both thermodynamics and kinetics can be modified

$NaAlH_4$@MOF has altered reaction pathway and accelerated desorption kinetics



$NaAlH_4$@Mg-MOF-74





(1) $NaAlH_4 \longrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2$ $\Delta H_d°(1) = 37$ kJ/mol $[H_2]$

(2) $1/3\ Na_3AlH_6 \longrightarrow NaH + 1/3Al + 1/2\ H_2$ $\Delta H_d°(2) = 23$ kJ/mol $[H_2]$

$$NaAlH_4 \xrightleftharpoons{[Cat.]} 1/3Na_3AlH_6 + 2/3Al + H_2 \xrightleftharpoons{[Cat.]} NaH + Al + 1/2H_2$$

Step 1 Step 2

Nano $NaAlH_{4@}$HKUST-1

Stavila et al. *ACS Nano* 2012, 6, 9807

R. K. Bhakta, V. Stavila, et al. *Phys. Chem. Chem. Phys.*, **14** (2012), 8160

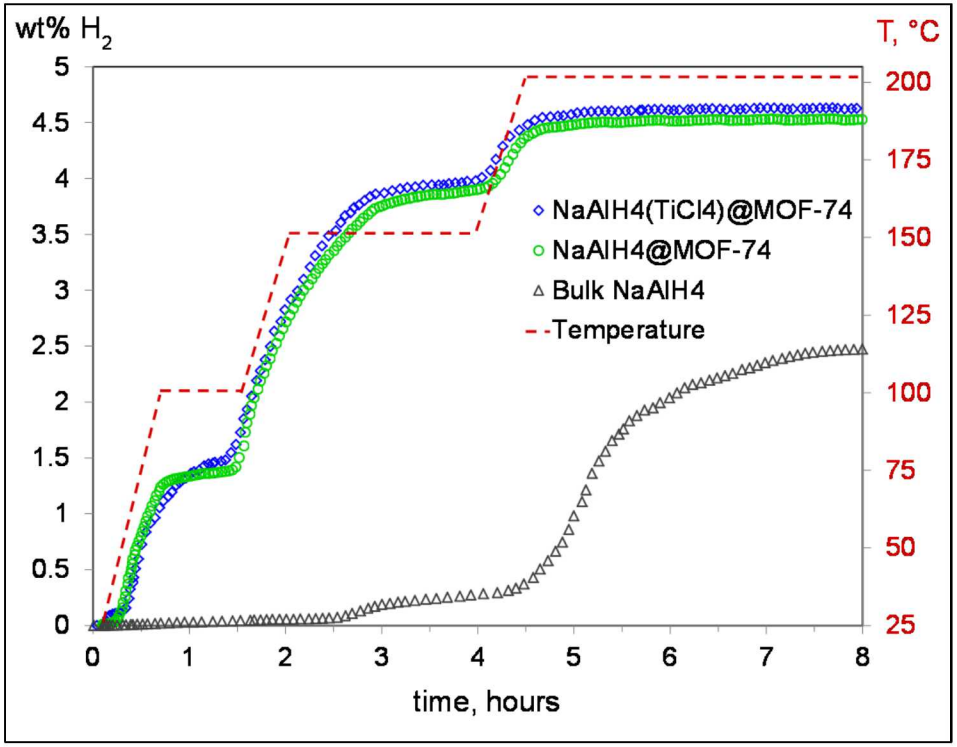
Temperature-programmed H_2 desorption

- **Highly improved kinetics vs bulk**
  - T_{onset} = ~30 ° C
- **Capacity almost 2X bulk at 200 ° C**
- **Ti does not affect H_2 desorption kinetics**

  → Difference almost entirely due to nanoscale and template effects

  → This is very different from bulk $NaAlH_4$
- **Initial desorption = 4.5 wt%**

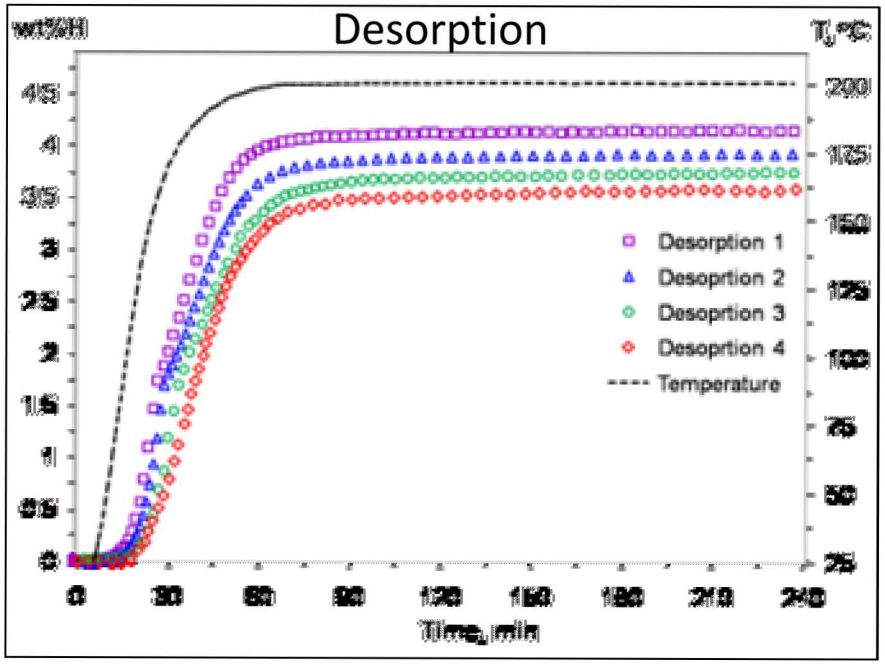
  → Nearly complete to NaH+Al

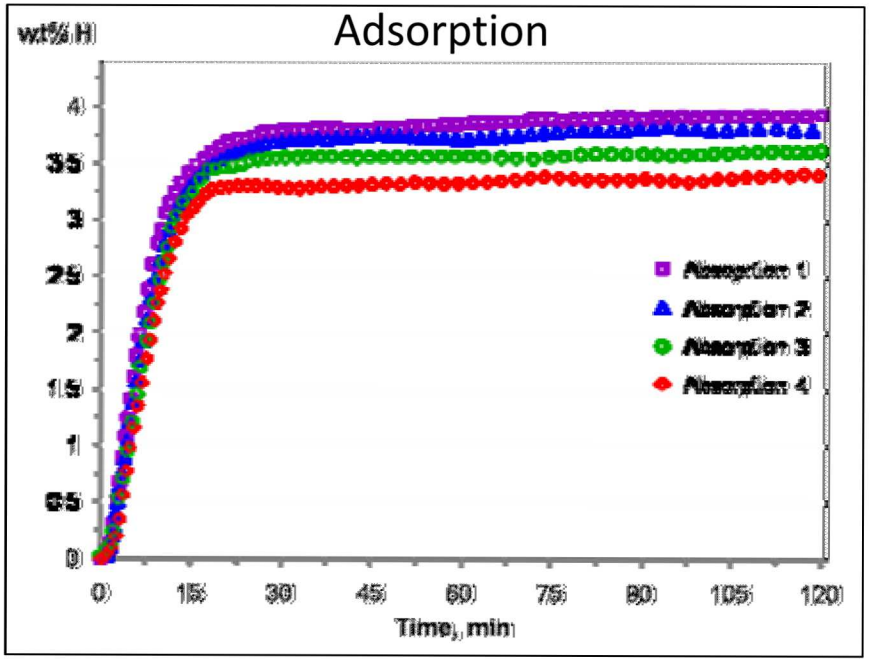


V. Stavila et al. *ACS Nano* 2012, **6**, 9807

$TiCl_x$ is essential for regenerating nano-$NaAlH_4$

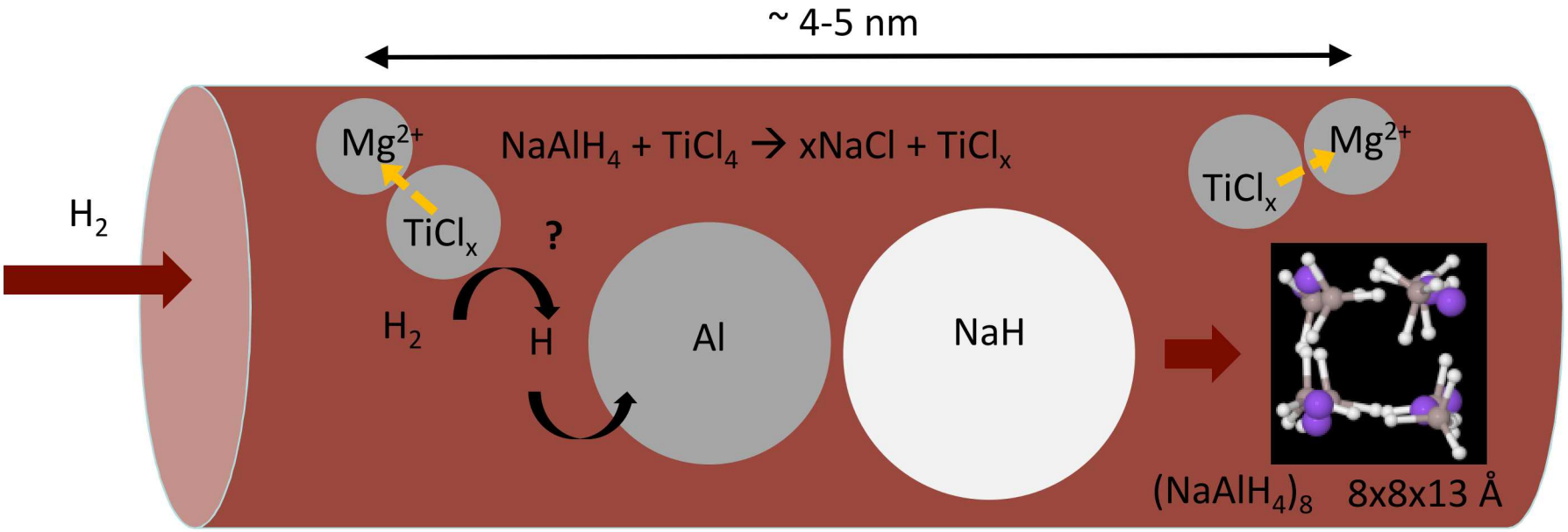
- <2.0 wt % uptake at 160 ° C under 10.5 Mpa (100 bar) H_2
- 4.5 wt% uptake with $TiCl_4$ doping
- Capacity decreases only ~15% in 4 cycles
- Compare with a carbon template:
  - 50% capacity loss in 4 cycles (T. Jensen *et al.*, *ACS Nano*, 2011)





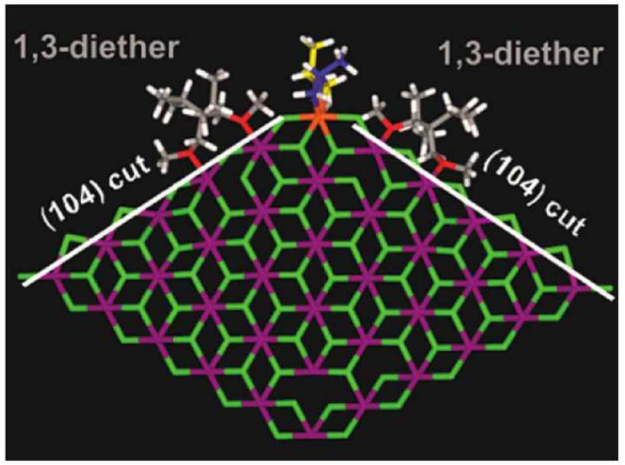
V. Stavila et al. *ACS Nano* 2012, **6**, 9807

What is the role of the Ti dopant in regenerating nanoconfined $NaAlH_4$?



$TiCl_4$@MOF-74 resembles "classical" Ziegler-Natta catalysts ($TiCl_4$@$MgCl_2$):

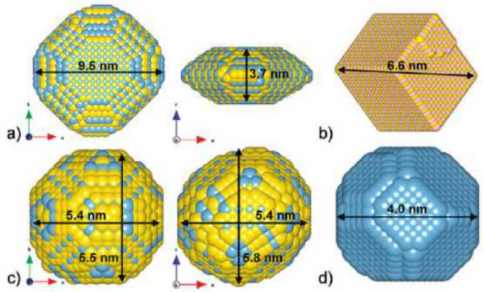
- $TiCl_4$ binds to unsaturated Mg^{2+} surface sites (4 or 5 coordinate)
- Titanium oxidation state: Ti(III) in both MOF and catalyst
- OMS in Mg^{2+} in MOF-74 is 5-coordinate



A. Correa et al. *Macromolecules* 2012, 45, 3695

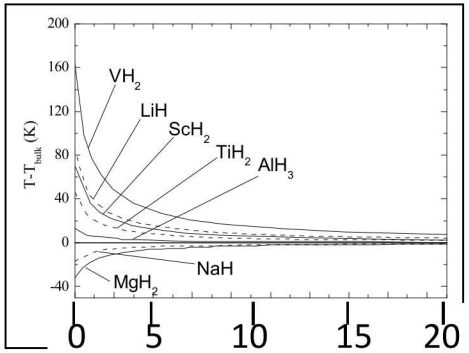
Theory suggests thermodynamics are affected only for extremely small particles

2-10 nm $NaAlH_4$ Clusters: 1-step reaction, no Na_3AlH_6 intermediate



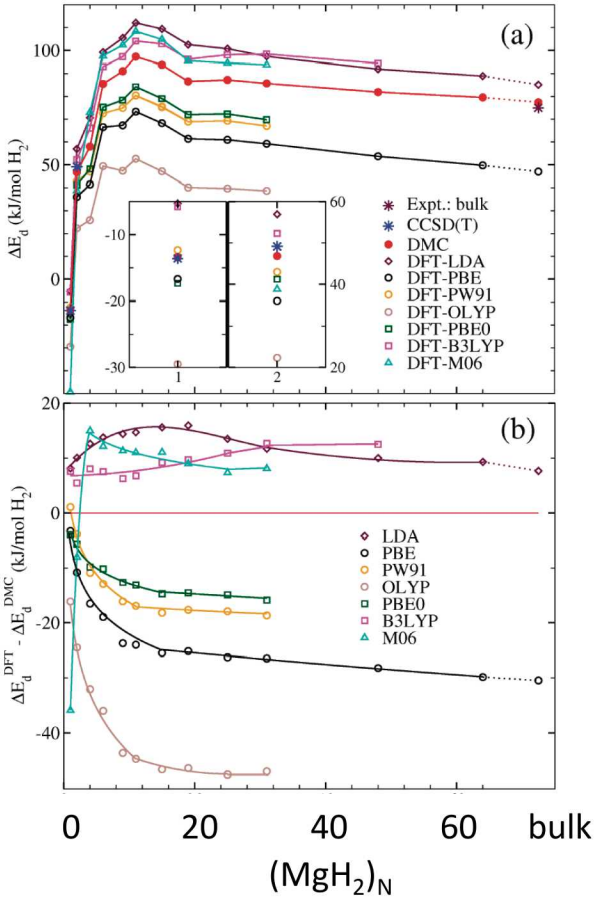
Mueller and Ceder
ACS Nano, **4**, 5647 (2010)

Hydride destablization as a function of particle size, predicted by Wulff construction



Kim, Johnson, Sholl
Nanotech., **20**, 204001 (2009)

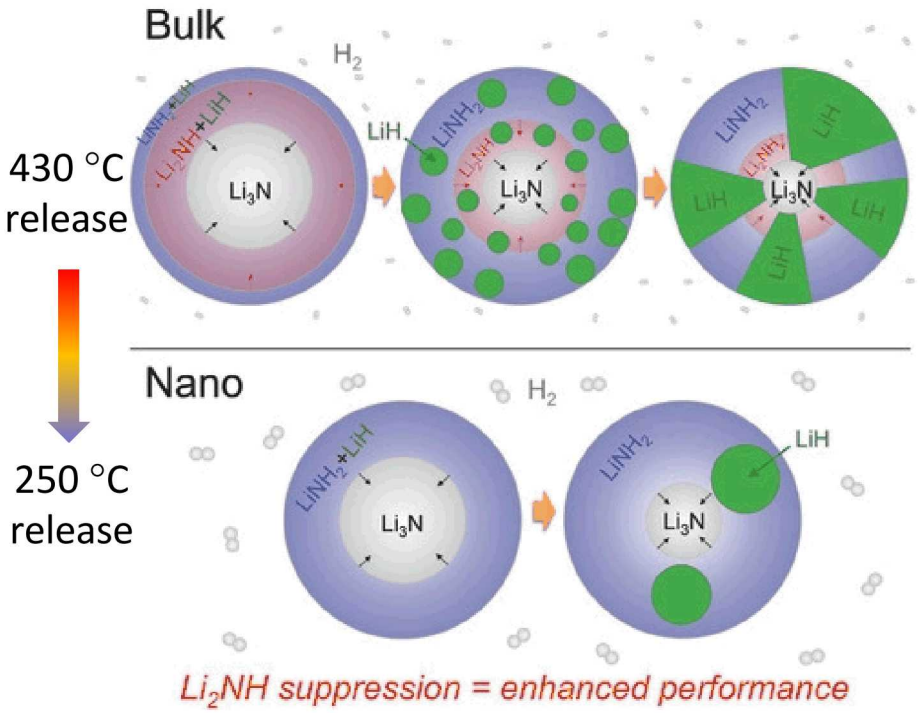
MgH_2 desorption energy predicted by QMC



Wu, Allendorf, Grossman
JACS, **131**, 13918 (2009)

How small can we get?

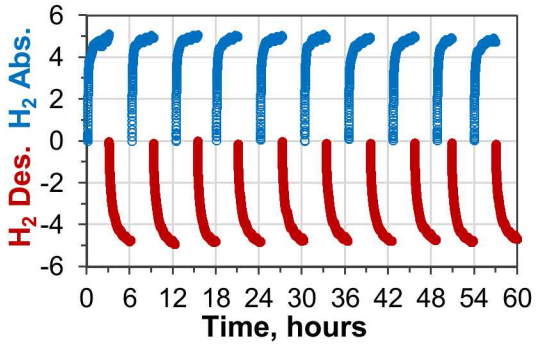
Nanoscale metal hydrides have faster H_2 uptake and release

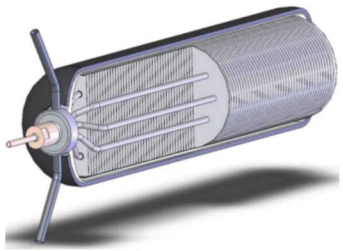


B. C. Wood *Adv. Mater. Interfaces* (2017)
https://doi.org/10.1002/admi.201600803

Metal Hydride Finite Element model reveals non-intuitive tradeoffs and benefits of using nanoscale metal hydrides in an operational H_2 storage tank

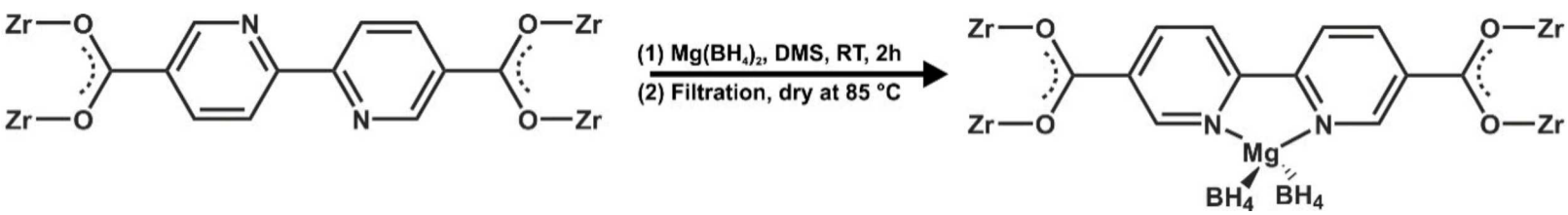
Design Parameters	bulk-Li_3N	KH-6nm-Li_3N
Reversible capacity. wt%	8.2	5.4
Thermal cond., W m^{-1} K^{-1}	1.0	9.6
Density of hydride bed, kg m^{-3}	710	760
Total system mass, kg	312	252
Total hydride mass, kg	112	116
Tank outer diameter, m	0.46	0.45
Tank length, m	2.21	2.19
System volume, m^3	0.256	0.227
% 2025 Gravimetric Target	33	40
% 2025 Volumetric Target	55	62





MHFE-SAH tank design

“Molecular” $Mg(BH_4)_2$? Non-innocent MOF hosts for metal hydrides

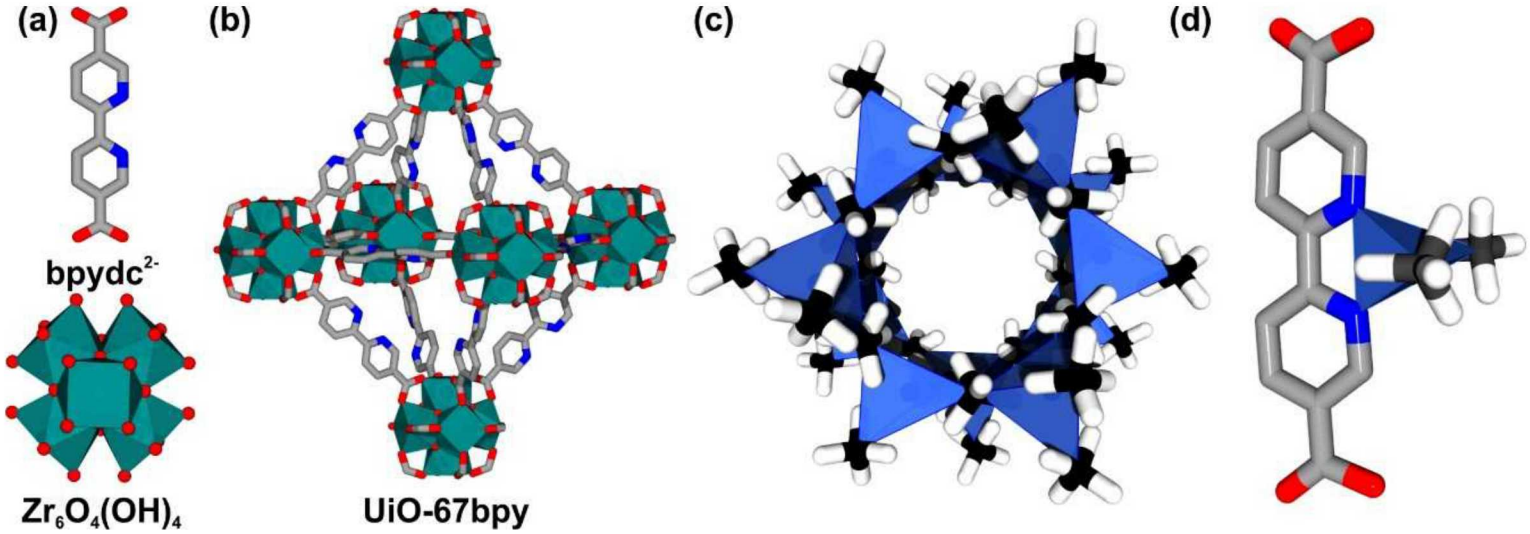


MOF building blocks

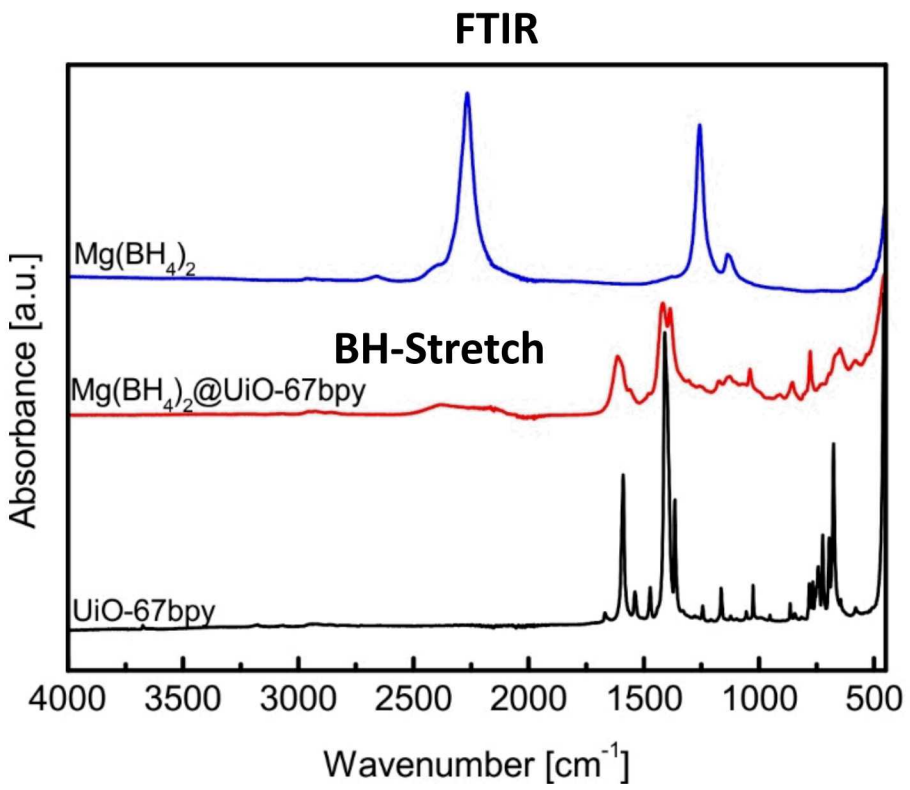
O_h pore

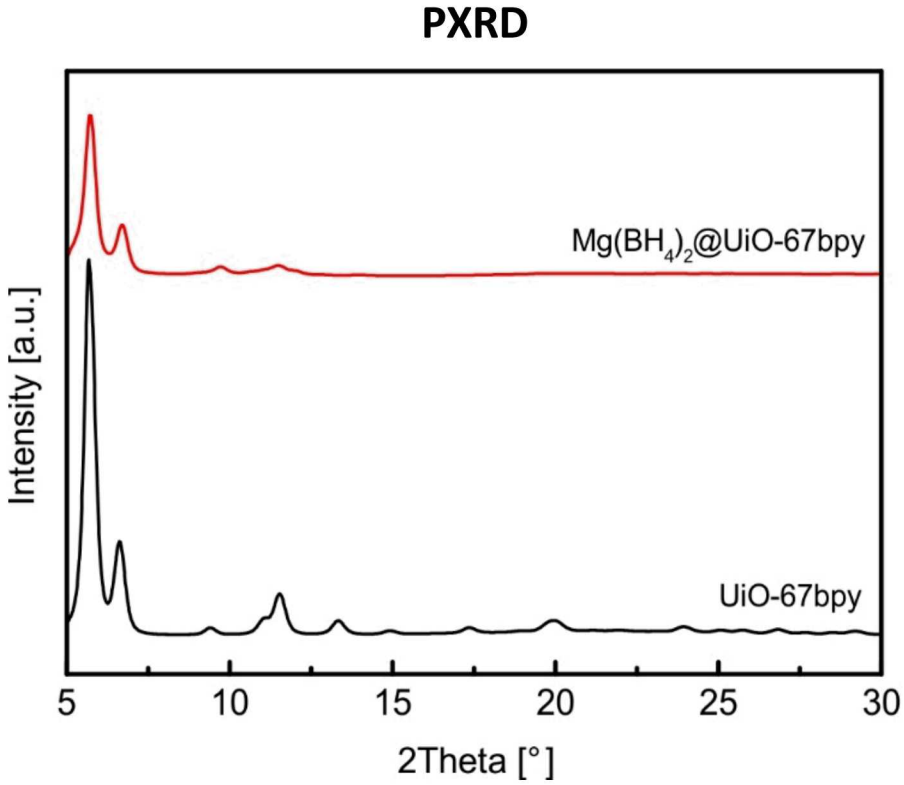
γ-$Mg(BH_4)_2$ fragment

$Mg(BH_4)_2$ coordinated $bpydc^{2-}$ linker



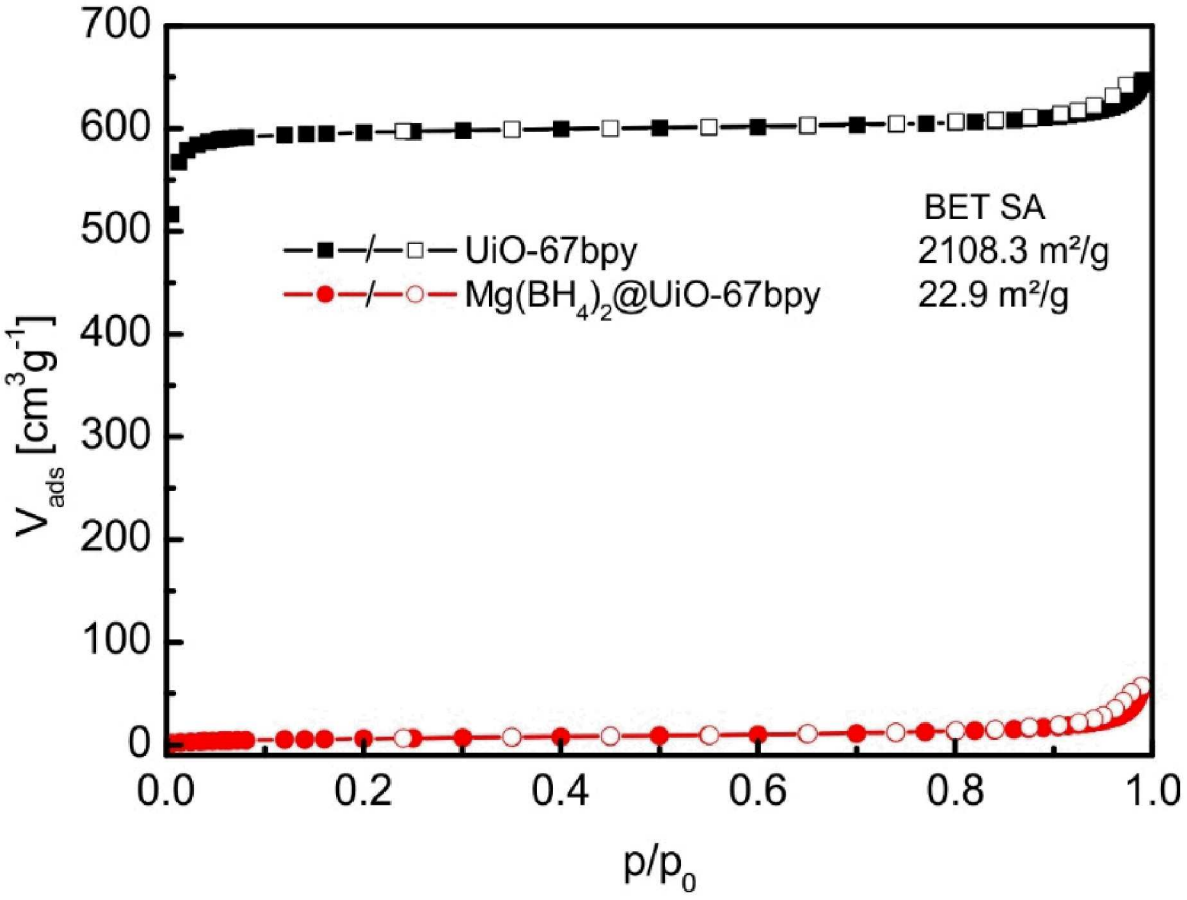
Installation of hydrides on chelating ligands





- **BH stretch visible after infiltration**
- **Slight decrease in cristallinity**

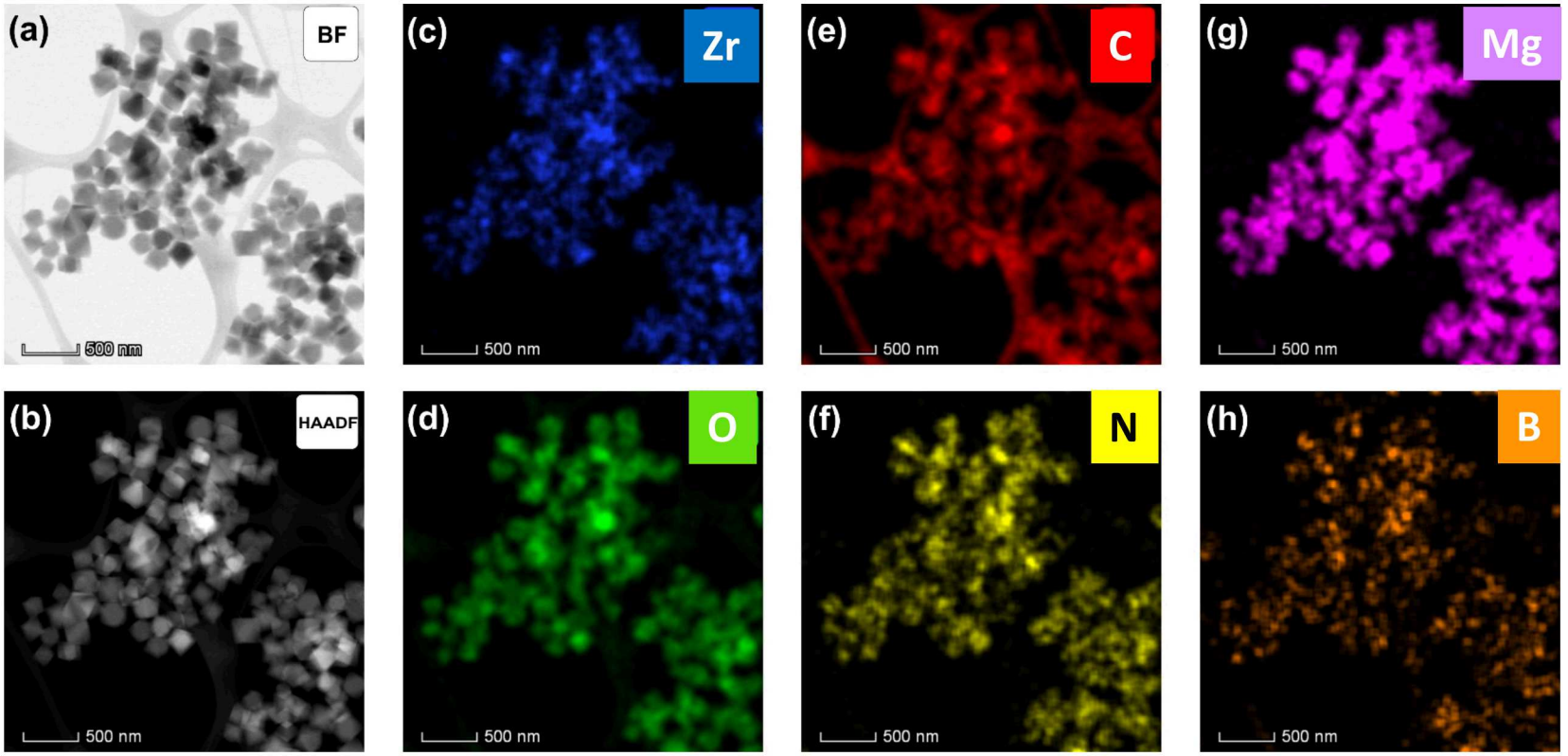
Hydride infiltration results in complete pore filling



- **$Mg(BH_4)_2$ occupy the pores fully**
- **Elemental Analysis suggests a formula of $[Mg(BH_4)_2]_{12}@Zr_6O_6(bpydc)_{12}$**

→ 1 hydride formula unit/chelating ligand

$Mg(BH_4)_2$ uniformly distributed throughout the crystals

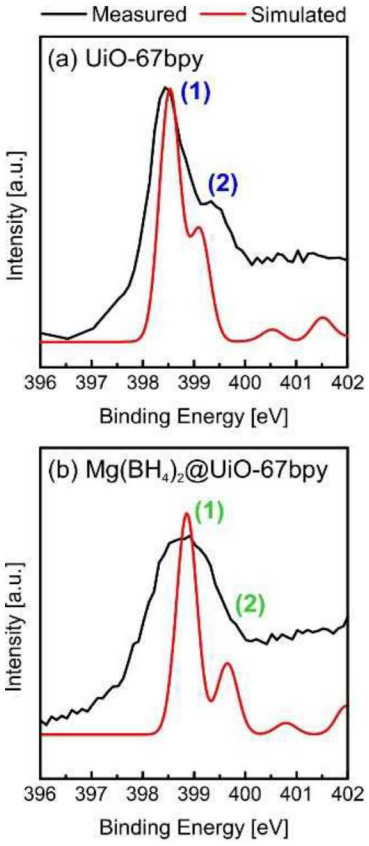


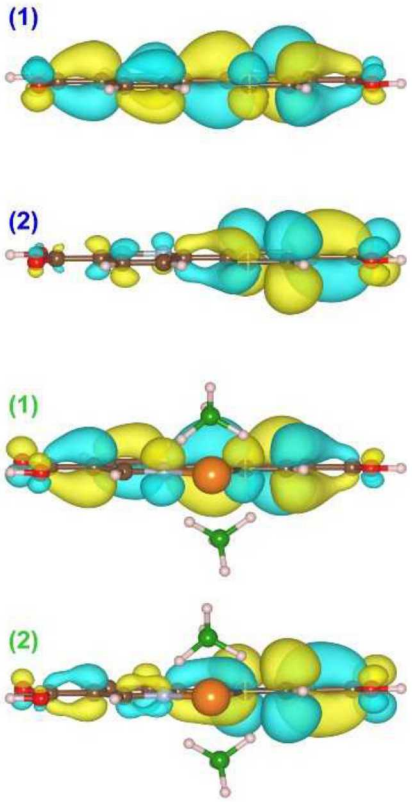
- No evidence of bulk hydride or hydride particles outside the pores
- EDS Spectrum rules out presence of S and Cl from precursors

X-ray Adsorption Spectroscopy confirms Mg-N coordination

N K-edge spectra fit well with simulated spectra

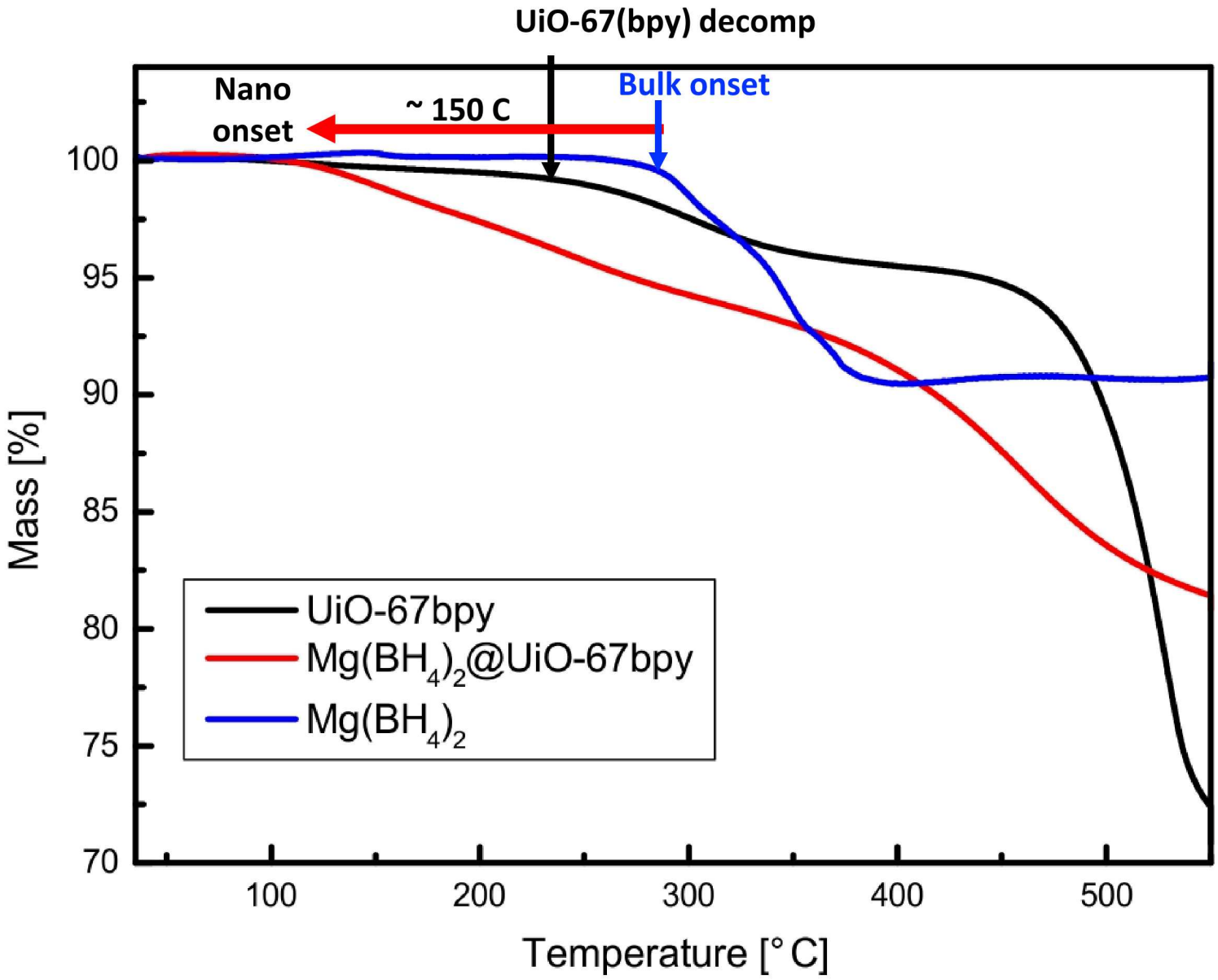
(1) = Delocalized excited π* state of H_2bpydc
(2) = Excited state localized on pyridyl N





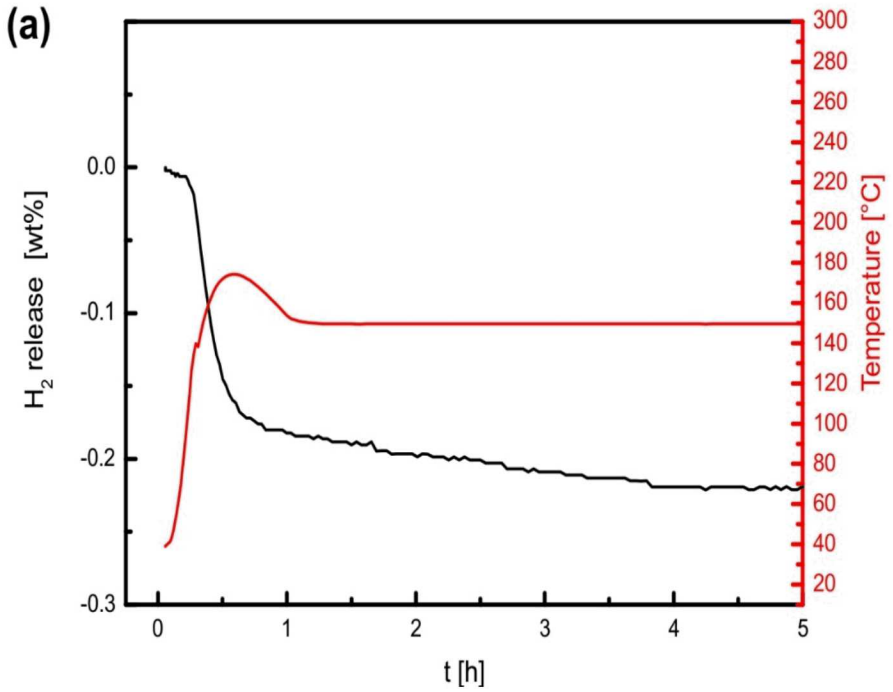
- **Shift of N K-edge (1) to higher energy consistent with Mg^{2+} coordination**
- **DFT calculations:**
  - **trans-bpy more stable than cis-bpy**
  - **$Mg(BH_4)_2$@bpy → cis is more stable**
  - **Hydride coordination increases bpy excited state delocalization → intensity decreases**

TGA supports DFT predictions, revealing H_2 release at much lower temperature compared to bulk

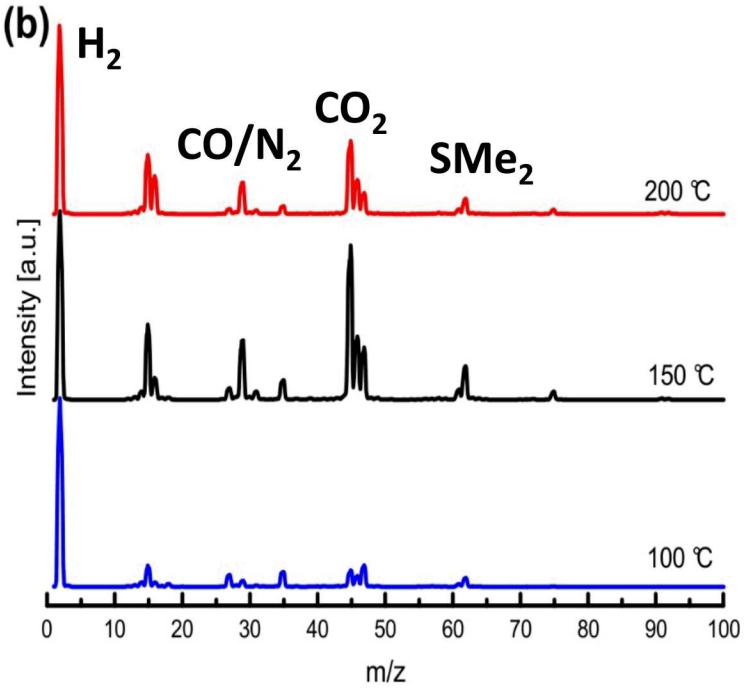


Material releases clean H_2 at low temperatures: reaction pathway altered (no B_2H_6 as in bulk)

Sieverts Measurement



Mass Spectrometry



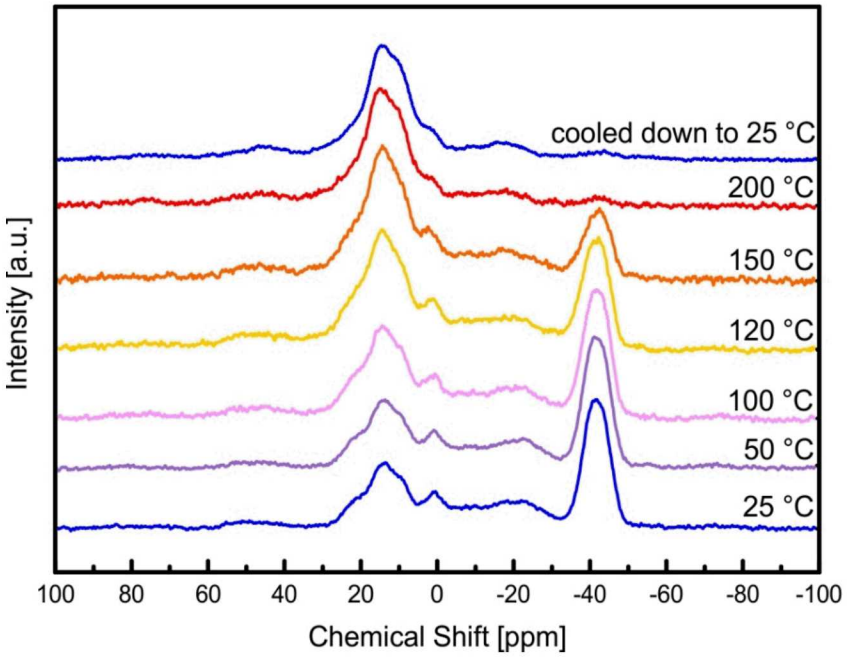
0.2 wt% H_2 released at 150 ° C

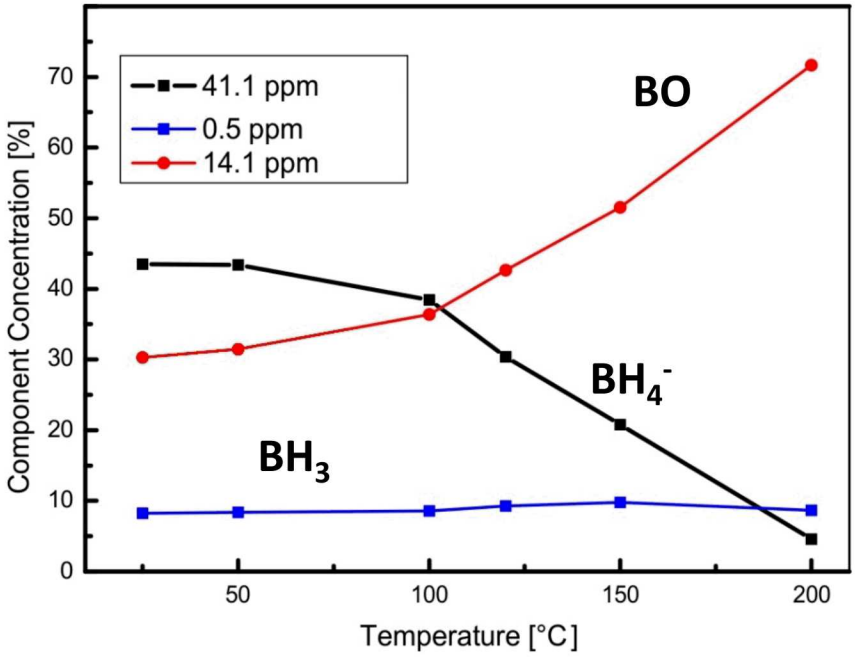
At low desorption T clean H_2 (Measurement not quantitative)

Material releases H_2, but also some decomposition of the framework occurs

MAS NMR shows that during dehydrogenation no $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ species are formed

^{11}B-MAS NMR



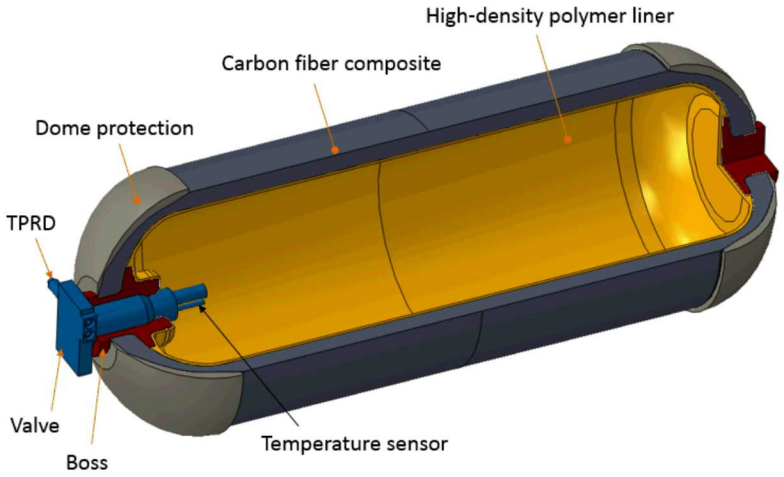


Signal at -41.1 ppm represents BH_4^-
Signal at 14.1 ppm represents BO species – interaction with ZrO cluster
Signal at 0.5 ppm represents BH_3 species

Take home lesson: "molecularizing" a complex hydride has a huge effect on the reactivity

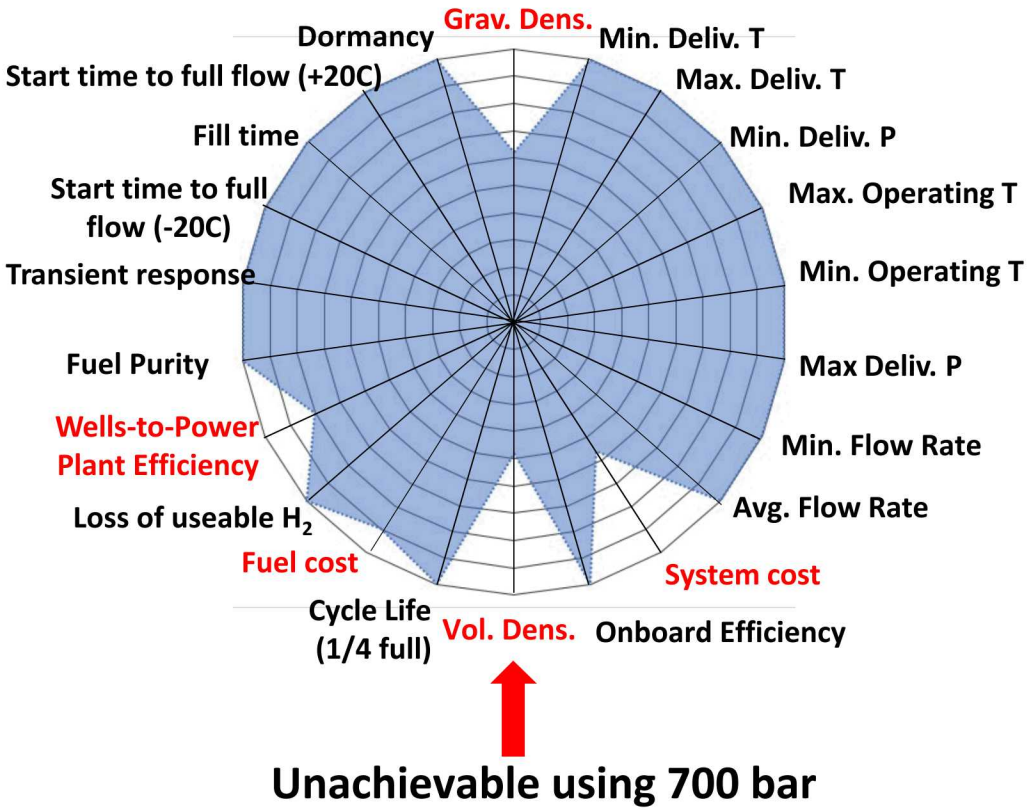
Although fuel cell vehicles are now commercially available, compressed H_2 storage falls short of several DOE targets

700 Bar Compressed Gas (2015 record) vs. revised DOE Ultimate Targets



TPRD = Thermally Activated Pressure Relief Device

Credit: Process Modeling Group, Nuclear Engineering Division. Argonne National Laboratory (ANL)



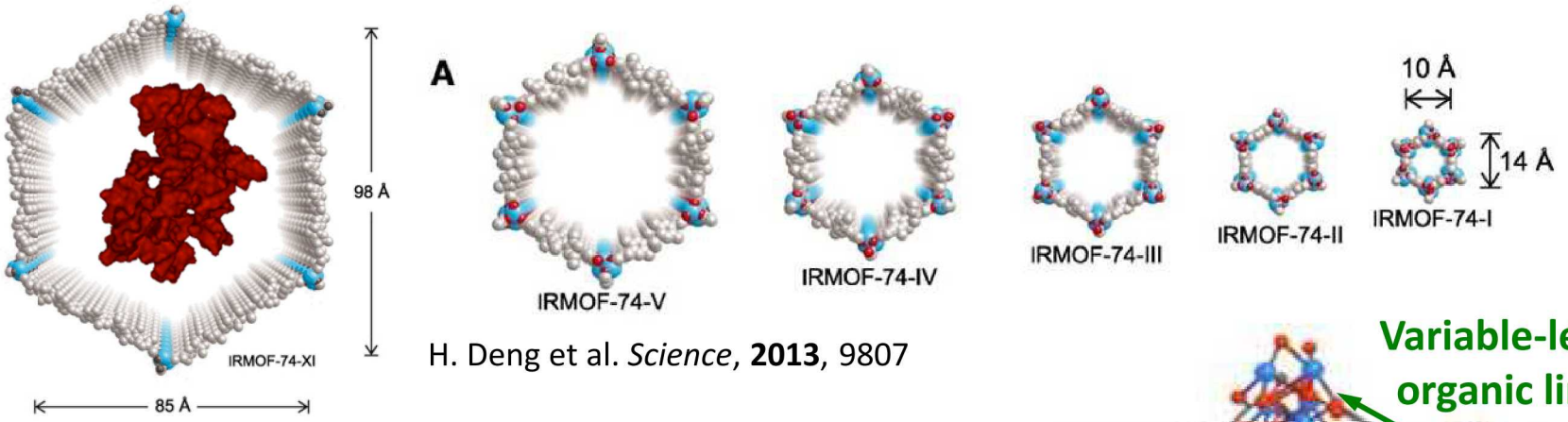
https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles

Hydrogen Carriers: MOF catalysts for releasing H_2 from alcohols and polyols

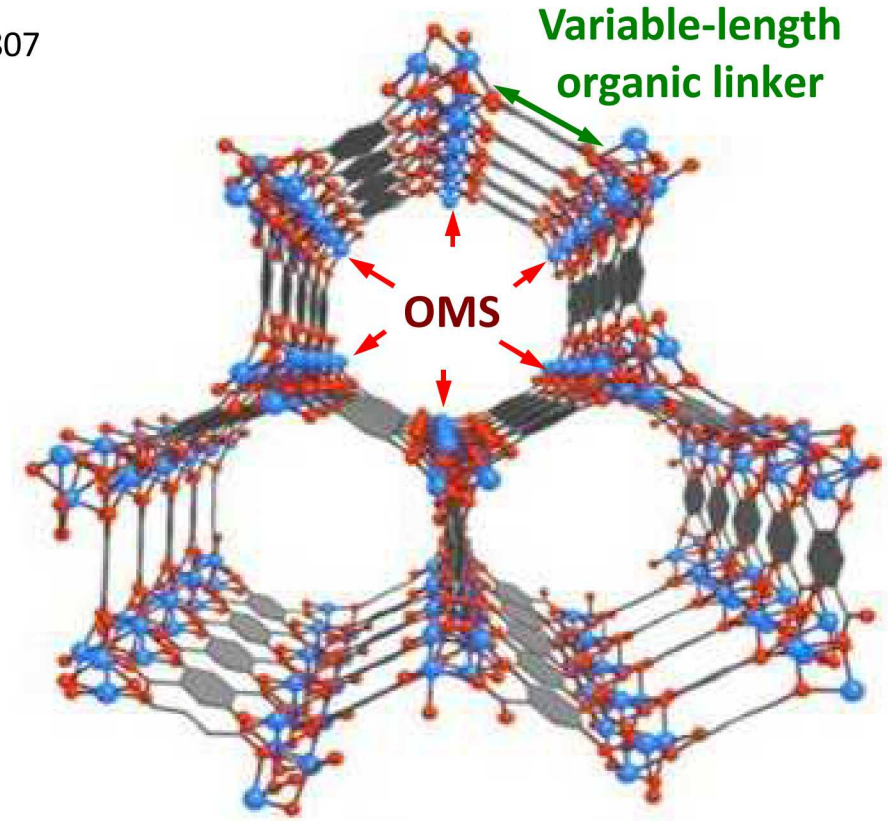
Efficient transport of hydrogen from point of production to fueling station is not possible using compressed gas:

- **1 kg H_2 = 1 gallon of gasoline (~4 L)**
- **Steel tubes: 280 kg per tanker**
- **Somewhat better: Composite tanks: 550 kg of hydrogen at 250 bar**
- **Typical gas station stores 75,000 – 230,000 L (20,000 – 60,000 gallons)**

IRMOF-74(Mg): A tunable host for metal hydride nanoparticles



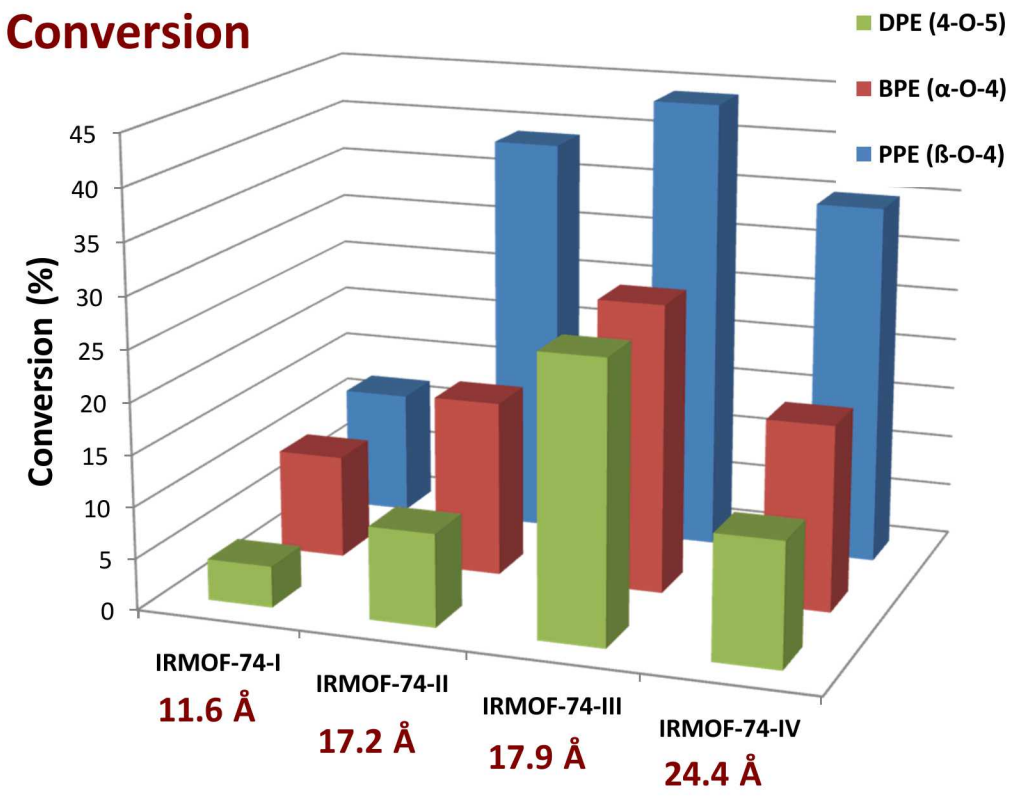
H. Deng et al. *Science*, **2013**, 9807

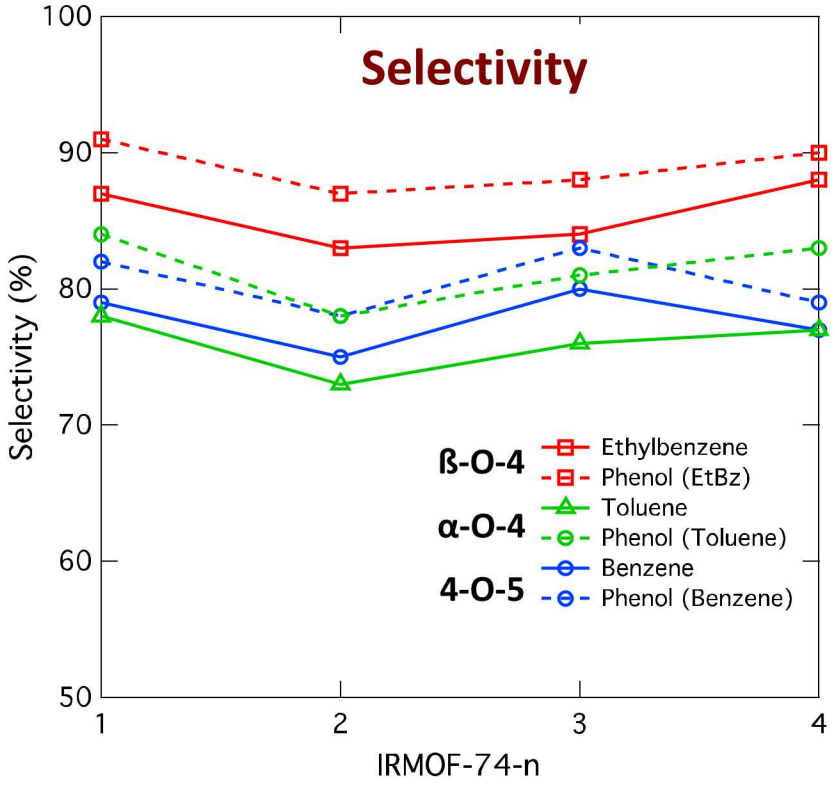


IRMOF-74-n(M)

- 1 – 10 nm 1-D channels
- Unsaturated metal coordination sites
- Variety of metal ions
- Tunable M^{+2} reactivity (Fe^{+2} vs. Mg^{+2})
- Largest pores can hold proteins such as GFP and myoglobin

IRMOF-74-n(Mg) is intrinsically catalytic for hydrogenolysis



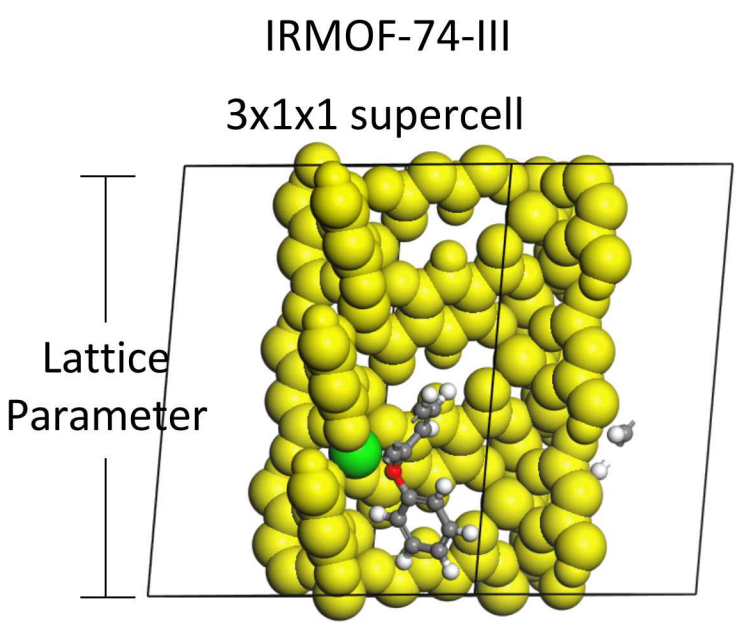


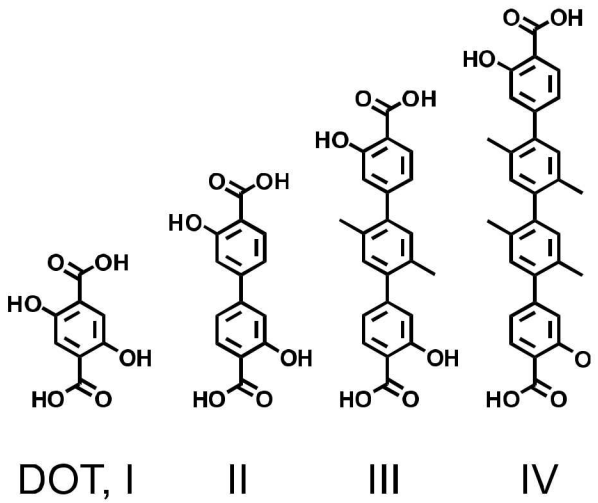
- Conversion trend: ß-O-4 > α-O-4 > 4-O-5
- Pore size effect: max conversion at IRMOF-74-III
- High selectivity: no ring hydrogenation or ring opening

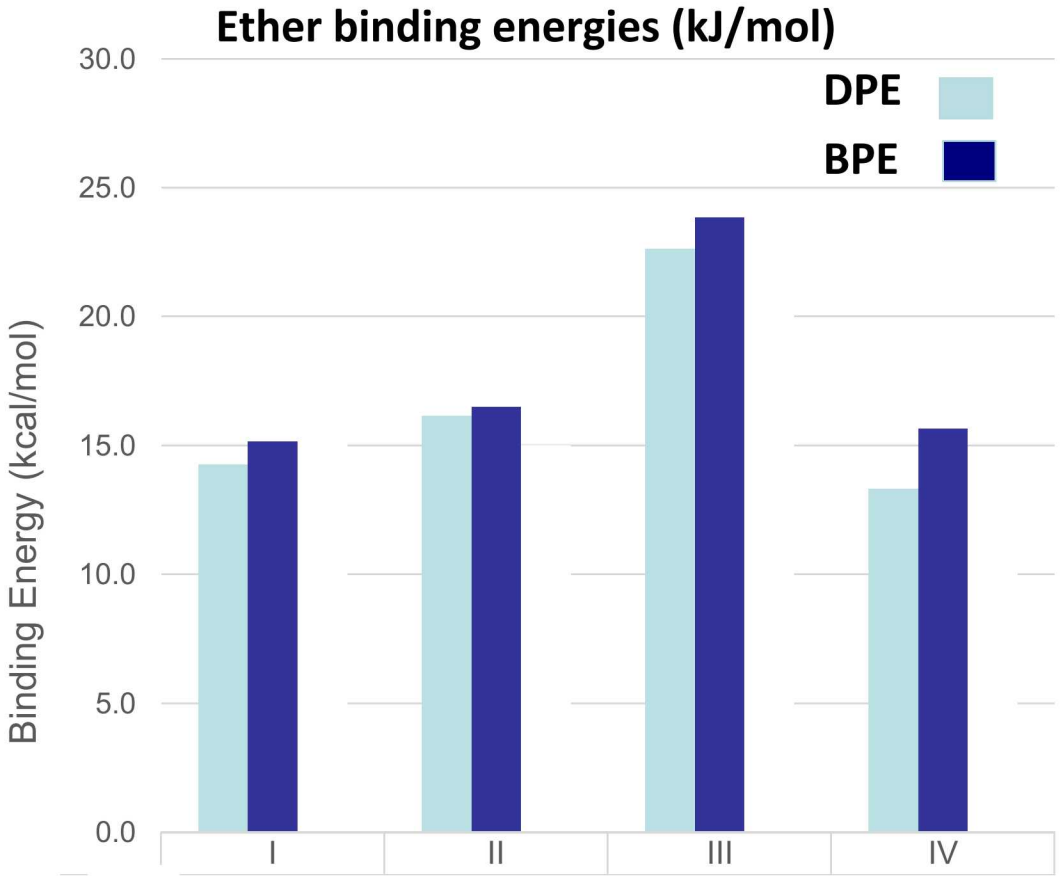
	Ring opening	PPE % Ring hydrogenation
IRMOF-74-1	0	1
IRMOF-74-II	0	1
IRMOF-74-III	0	1
IRMOF-74-IV	0	2

V. Stavila et al. *Chem. Sci.* 2019 DOI: 10.1039/C9SC01018A

Aryl ether binding to IRMOF-74-III is significantly stronger than IRMOF-74-(I, II, or IV)







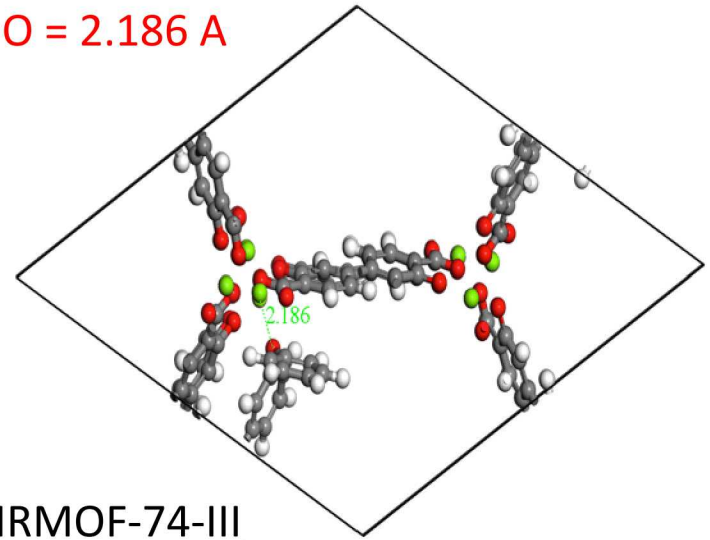
	IRMOF-74(I)	IRMOF-74(II)	IRMOF-74(III)	IRMOF-74(IV)
DPE	59.7	59.1	94.7	55.8
BPE	63.4	69.1	99.8	65.6
PPE	64.2	73.6	98.1	71.0
Phenol	63.7	75.4	117.3	69.1

V. Stavila et al. *Chem. Sci.* 2019 DOI: 10.1039/C9SC01018A

The Mg(II)-O(ether) bond distance is also shorter in IRMOF-74-III, consistent with stronger binding

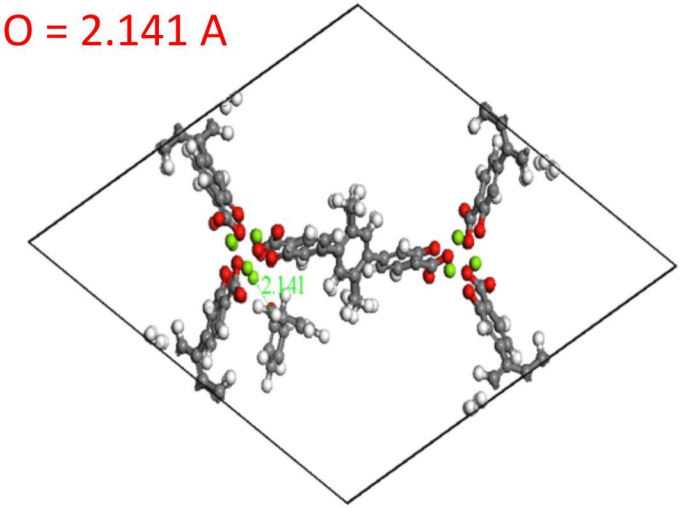
4-O-5@IRMOF-74-II

Mg(II)—O = 2.186 A

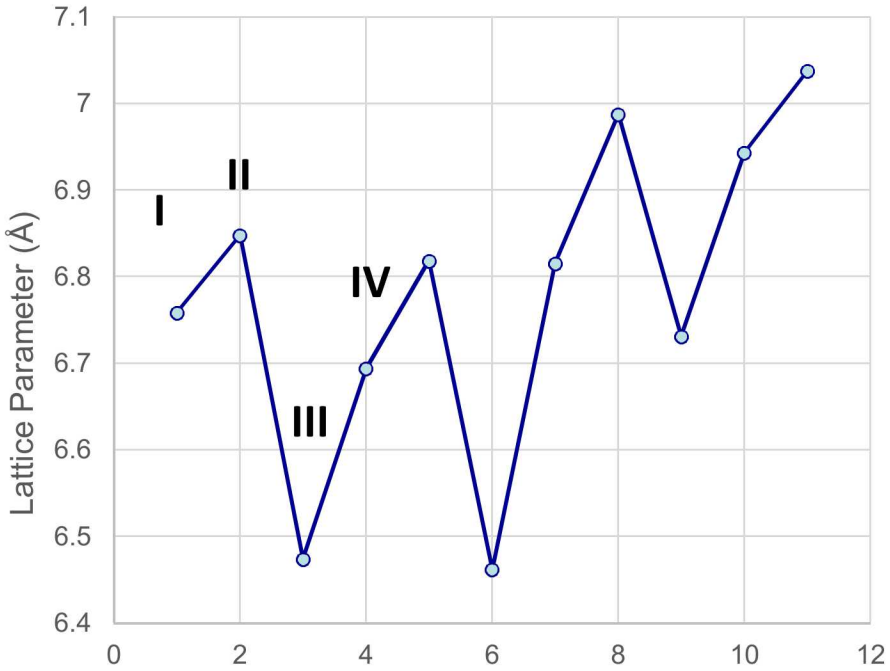


4-O-5@IRMOF-74-III

Mg(II)—O = 2.141 A

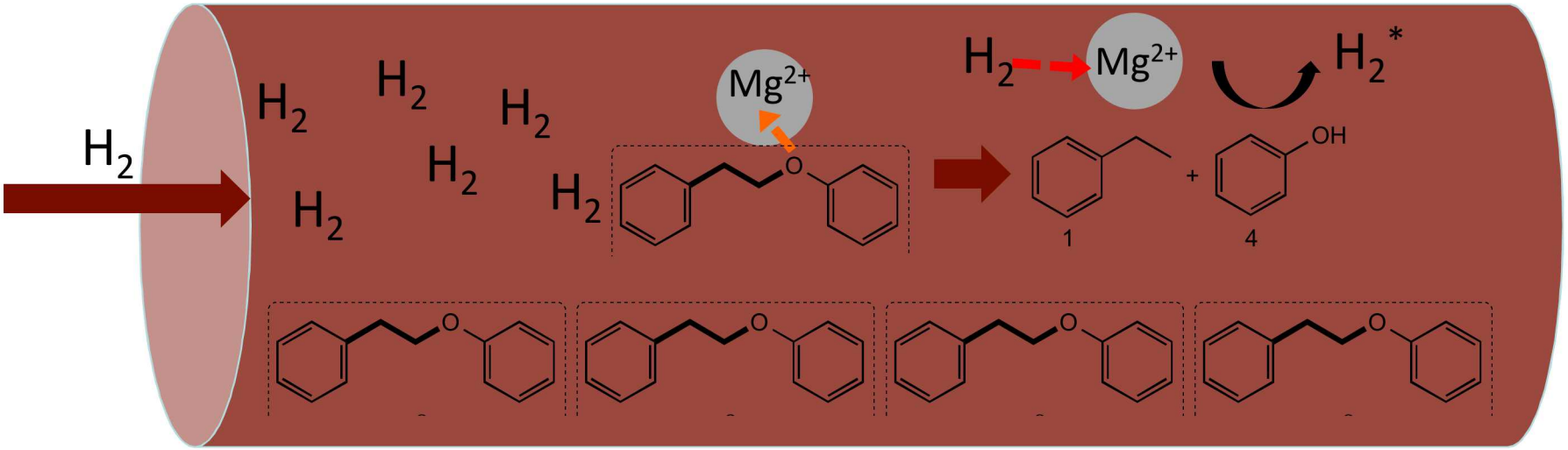


Lattice parameter of 4-O-5@IRMOF-74-n



V. Stavila et al. *Chem. Sci.* 2019 DOI: 10.1039/C9SC01018A

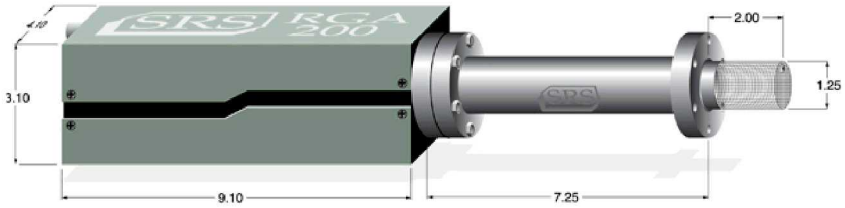
Proposed mechanism of hydrogenolysis and the role of the Mg(II) open metal site



Proposed mechanism:

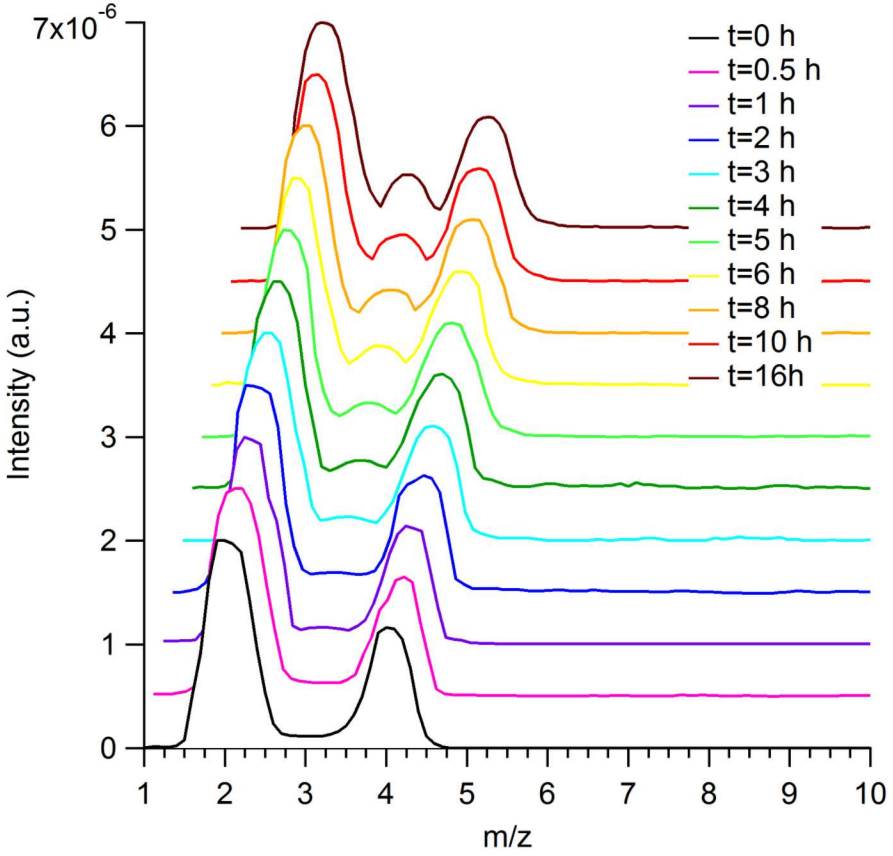
- OMS in Mg^{2+} in MOF-74 is 5-coordinate Lewis acid
- H_2 Qst (77K) by Mg_2(dobdc): 10. 6 kJ/mol
- Computed Q_{st} for PPE: ~70 kJ/mol (I, II, IV); ~100 kJ/mol (III)

H_2/D_2 Exchange in MOF-catalyzed hydrogenolysis reactions



Residual Gas Analyzer

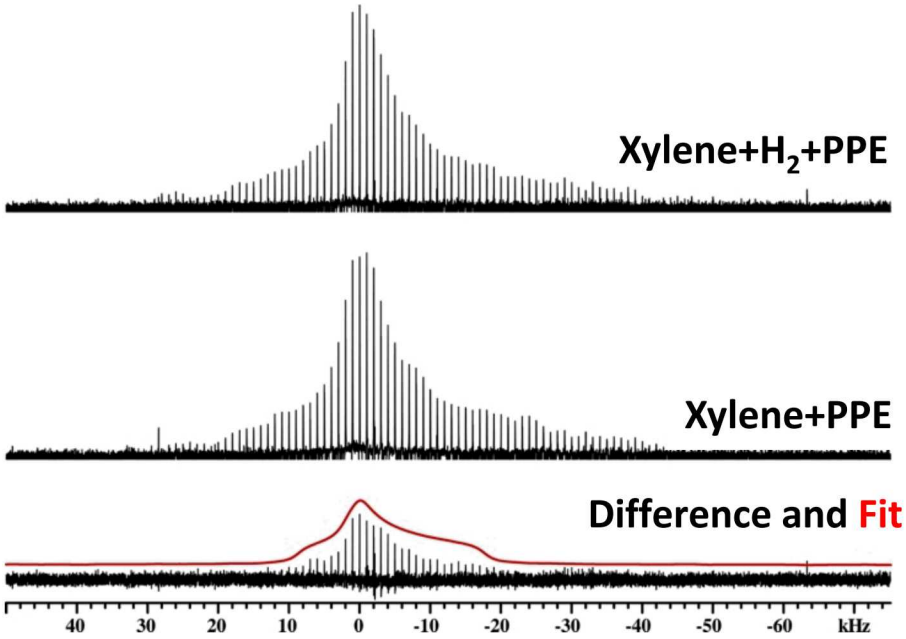
Sandia RGA setup

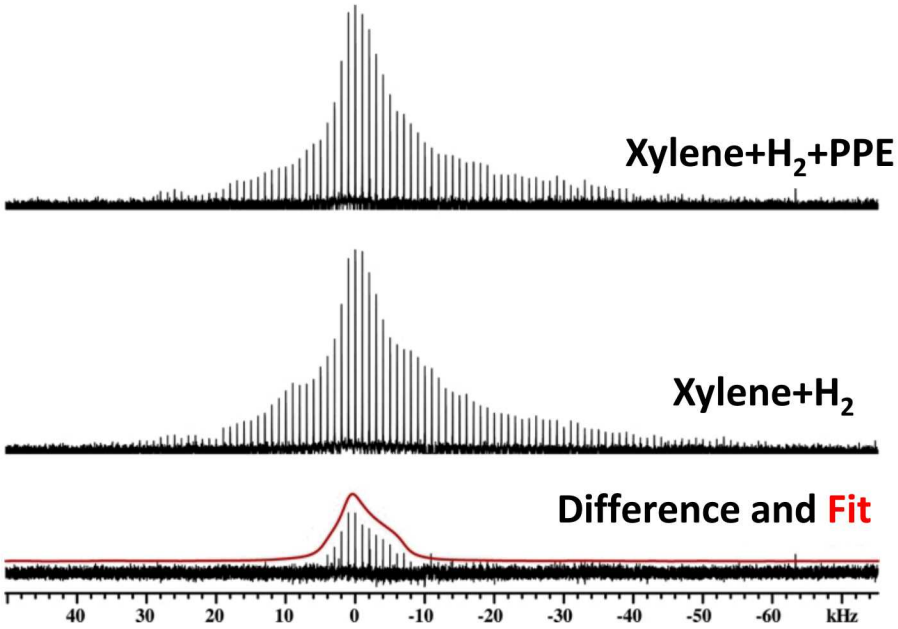


H-D isotope exchange experiment (at 120 ° C) showing the formation of HD (m/z=3) in p-xylene in the presence of Mg-MOF-74

IRMOF-74(I): Solid-state ^{25}Mg NMR indicate that both H_2 and ether molecules interact with the Mg(II) OMS

- 1.5 MPa H_2
- ^{25}Mg natural abundance
- Double frequency sweep/Quadrupole Carr-Purcell-Meiboom-Gill (QCPMG) detection

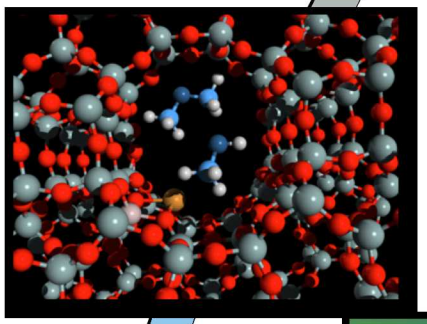




	C_q (DFT)	η_q (DFT)	C_q (exp.)	η_q (exp.)
IRMOF-74(I)Mg	11.98	0.59	7.7	0.70
IRMOF-74(I)Mg + H_2	10.69	0.64	4.8	1.00
IRMOF-74(I)Mg + PPE	−6.75	0.85	3.1	1.00

MOF-catalyzed upgrading of biomolecules

Biomass Indirect Liquefaction
Light oxygenate intermediates



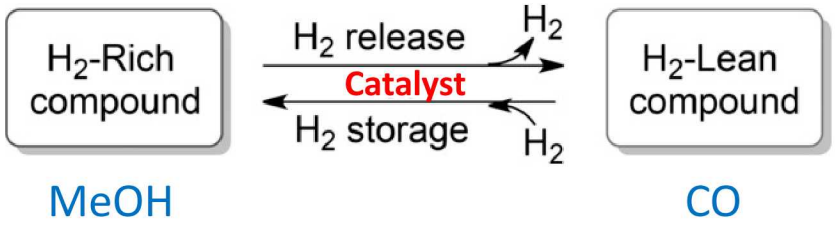
Multi-functional catalysts for unique transformations
Balancing acidic, basic, metallic sites

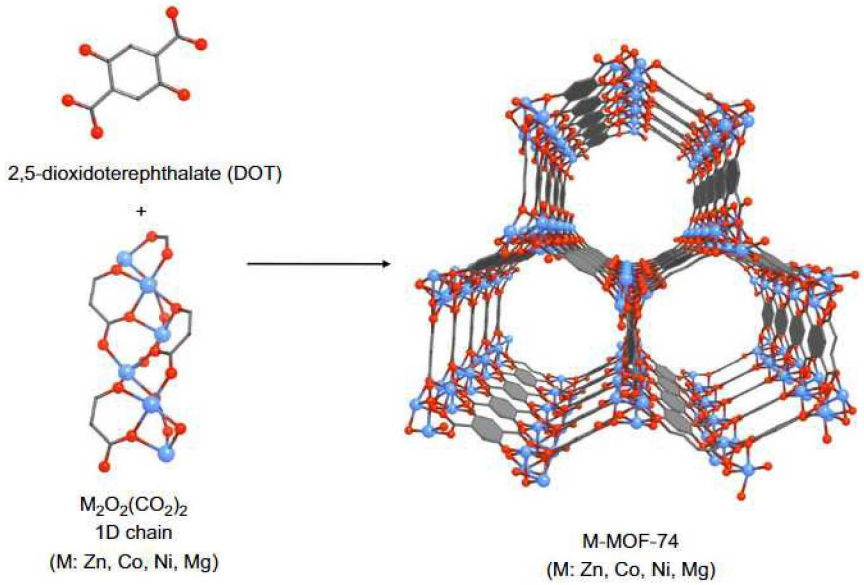
Suite of biofuels and co-products to meet market demand
High-octane gasoline, distillate fuels, and polymer precursors

Image courtesy of D. Ruddy, NREL

MOF Catalysts for Hydrogen Storage in LOHCs

- **Liquid organic hydrogen carriers**
  - Improved storage/transportation over gaseous hydrogen
  - With an appropriate catalyst, hydrogen can be reversibly produced on demand
- **Metal organic frameworks (MOFs)**
  - Open metal sites (OMS) can be catalytically active
  - Homogeneously dispersed reactive centers
  - High porosity and surface area
  - Tunable structure
- **Methanol dehydrogenation to explore potential of MOFs as dehydrogenation catalysts**



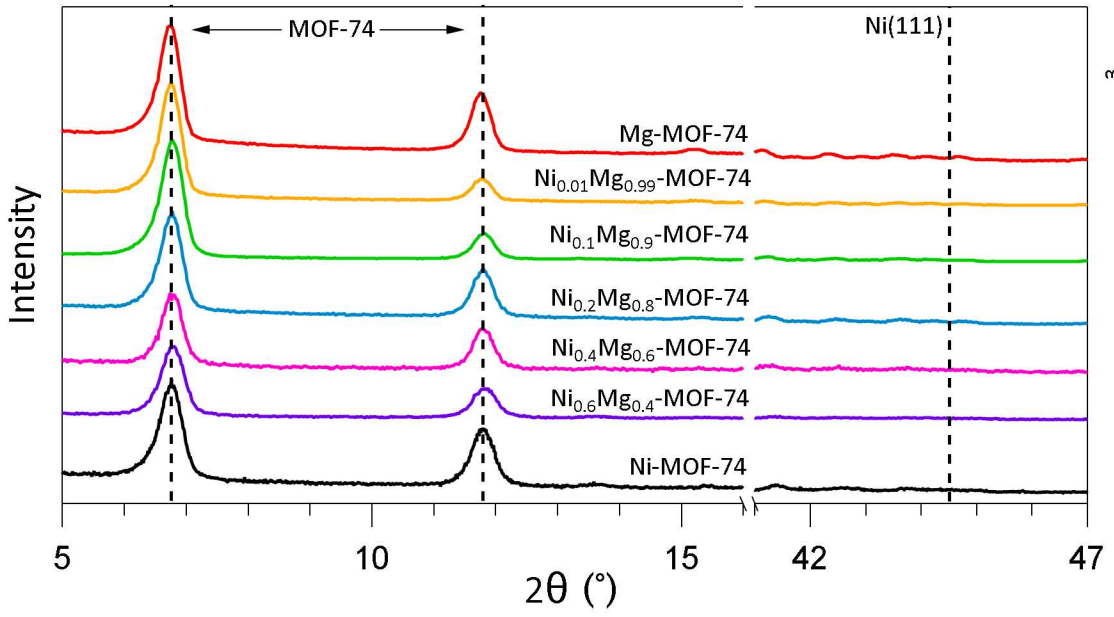


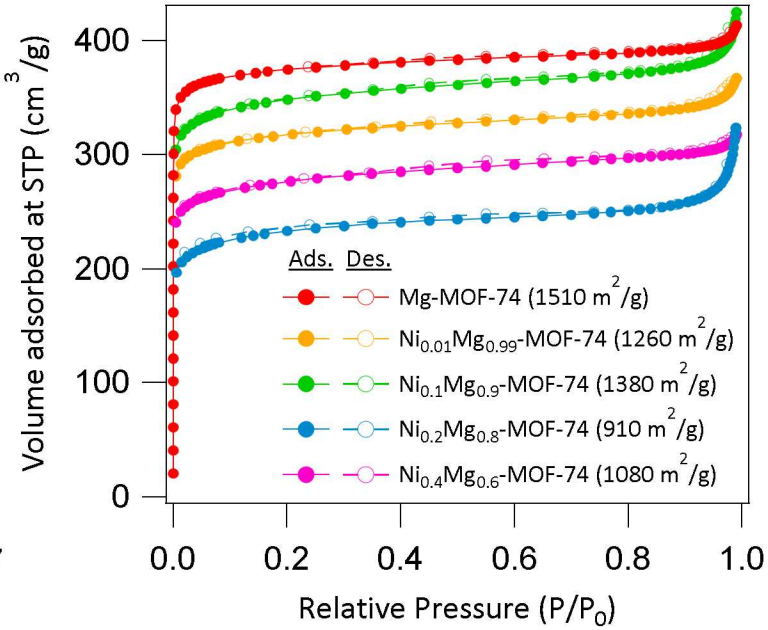
Top: Xie, Y., et al. *Angew. Chem. Int. Ed.* 2019, 58, 5105-5109
Bottom: Glover, T.G., et al. *Chem. Eng. Sci.* 2011, 66, 163-170

Catalyst series: Ni_xMg_{1-x}-MOF-74

- **MOF-74 is promising for dehydrogenation:**
  - Adsorbs MeOH
  - Catalyzes MeOH-activated H_2O dissociation
    - G. Flores et al. *Appl. Sci.-Basel* **8** (2018), 270
- **Synthesis of Ni_xMg_{1-x}-MOF-74**
  - React solution of $MgCl_2$, $NiCl_2$, and DHTA in DMF/EtOH/H_2O at 120 °C
  - Wash product then activate at 170 °C in vacuo
- **Characterization reveals a similar structure across the samples**
  - MOF-74 crystal structure with high surface area of 910-1510 m^2/g

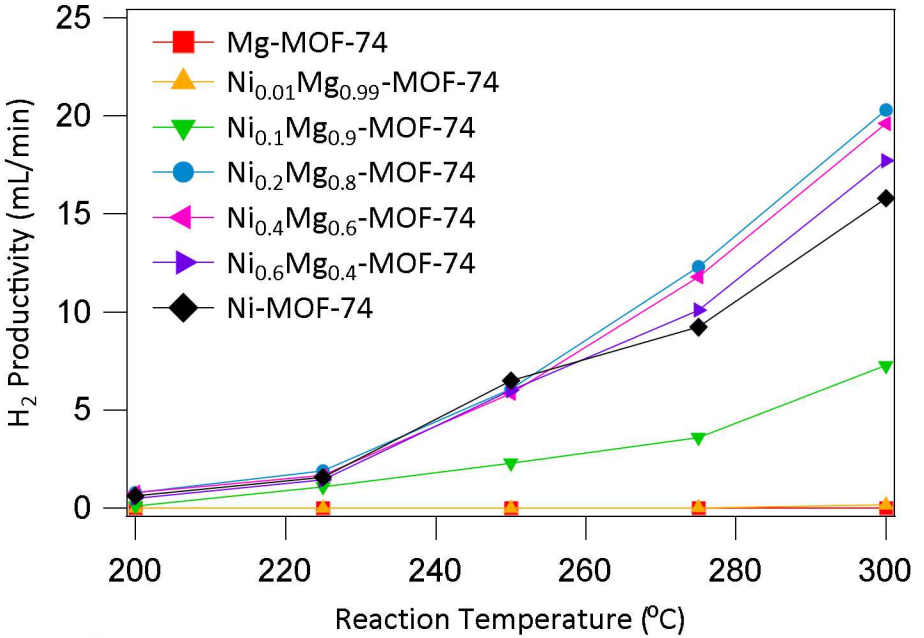
1% Ni 10% Ni 20%Ni

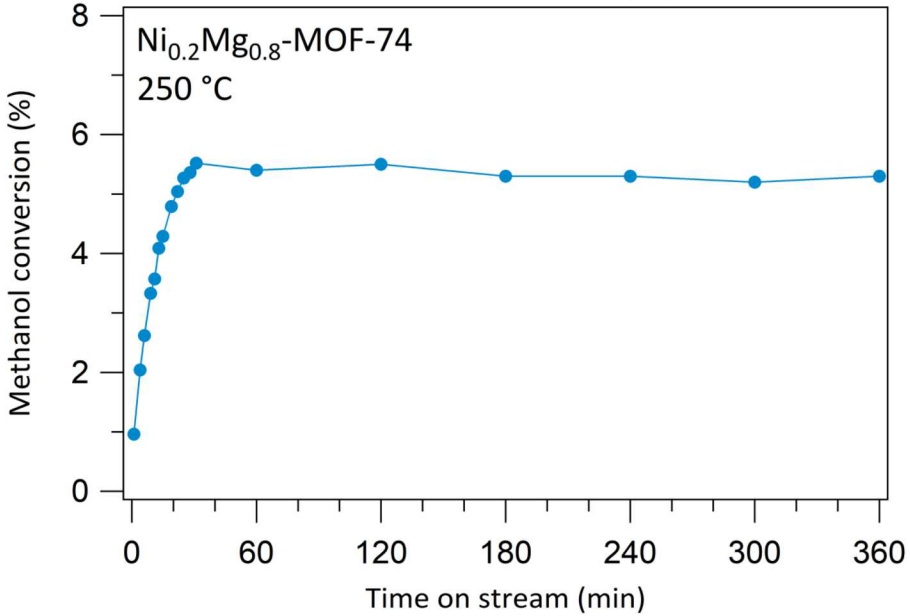




MeOH dehydrogenation on Ni_xMg_{1-x}-MOF-74

- **Mg-MOF-74 is inactive for MeOH dehydrogenation**
- **The addition of Ni improves catalyst activity**
  - Above 250 °C, H_2 productivity is maximized by an intermediate Ni content (20-40%)
- **Catalyst performance is stable after a brief activation period**
- **Conversion can be increased up to 100% by lowering the space velocity**





Test conditions:

1 bar

35 sccm N_2, 55 sccm MeOH vapor

100 mg catalyst, diluted with sand

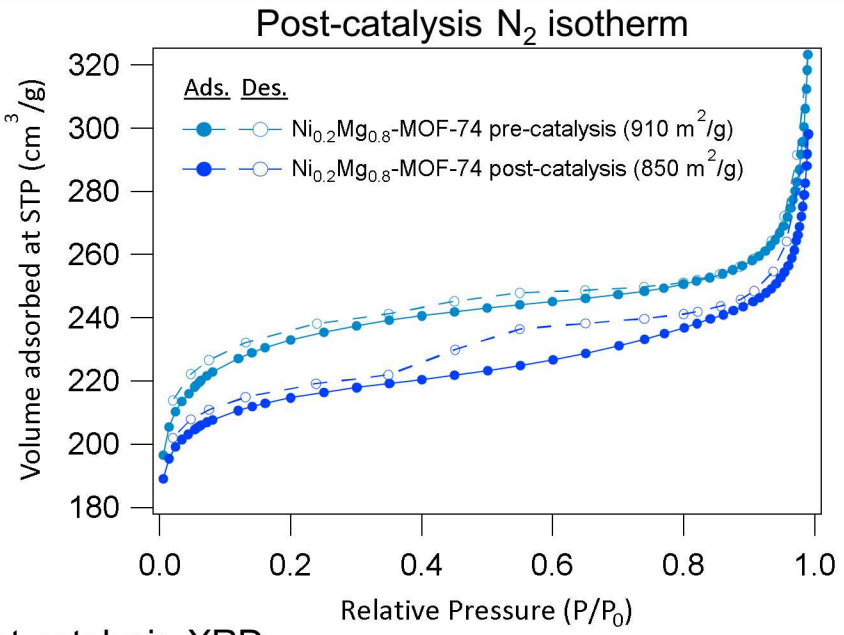
Products consist solely of H_2 and CO

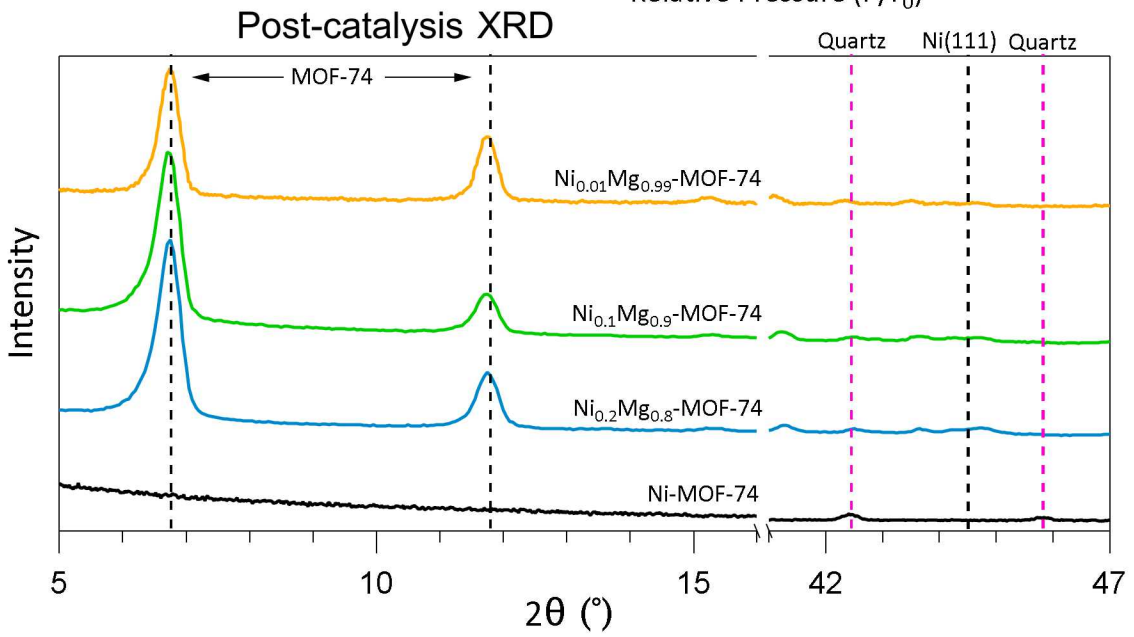
Catalyst testing performed by Dr. Ji Su, LBNL

Structural stability of bimetallic MOF-74 after reaction

- **The high surface area MOF-74 framework is maintained post-catalysis in the bimetallic MOF materials**
  - Hysteresis indicates a change in porosity
- **Mg helps to stabilize the MOF-74 structure under methanol dehydrogenation conditions**
  - Without the addition of Mg, Ni-MOF-74 is unstable under these conditions
  - No peaks for Ni(111) are observed; however, highly dispersed particles are possible
- **Future work includes APXPS to probe the active Ni sites**

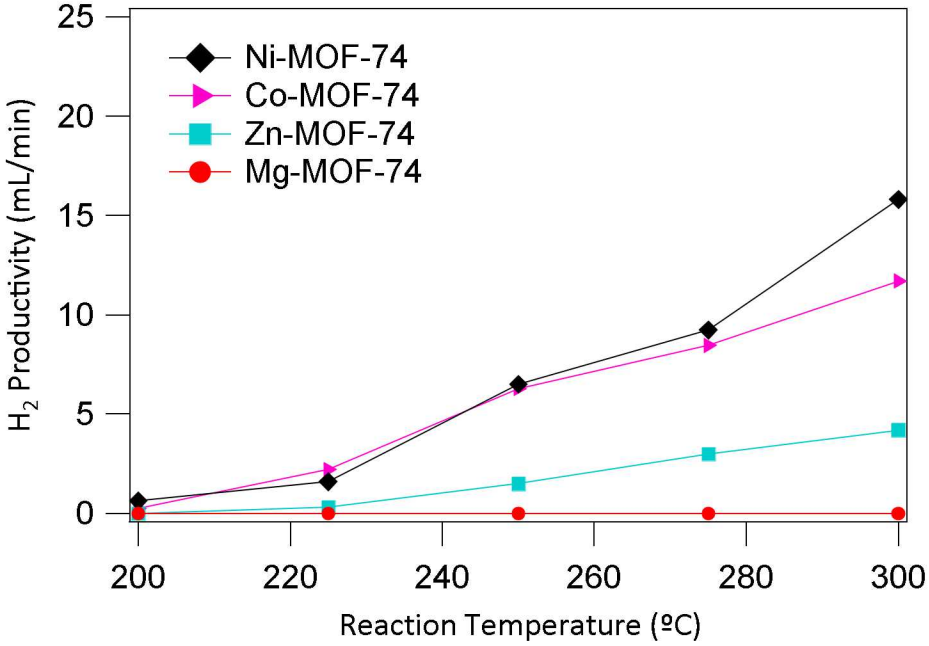
Bimetallic compositions balance the stability of Mg-MOF-74 with the activity of Ni-MOF-74



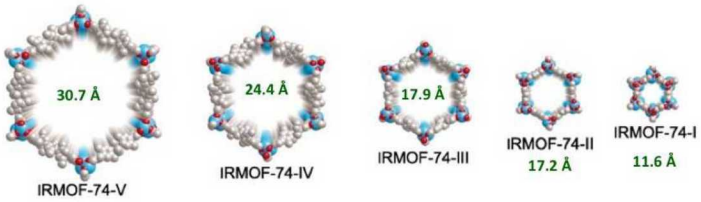


Tunable catalyst design with MOF-74

- **The MOF-74 framework can incorporate many metals as open metal sites (OMS)**
  - Co-MOF-74 shows comparable performance to Ni-MOF-74
  - Other transition metals possible



- **Pore size can also be tuned as a parameter by varying organic linkers**
  - **Deng, Yaghi et al. *Science* 2012**



- **Our current research is considering MOF catalysts for the reversible dehydrogenation of other LOHCs**
  - e.g. ethylene glycol and other polyols

Acknowledgements

Sandia National Labs
- Dr. Josh Sugar (TEM)

Pacific Northwest National Lab
- Dr. Andy Lipton (NMR)

Aarhus University
- Mathias Jørgensen (metal hydrides)

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- Dr. Ji Su (catalyst testing)
- Prof. Gabor Somorjai
- Dr. Jinghua Guo (ALS)
- Dr. Yi-Sheng Liu (ALS)

Lawrence Livermore National Lab
- Dr. Brandon Wood
- Dr. Liwen Wan

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International Congress Center

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Call for Papers will start in October 2019

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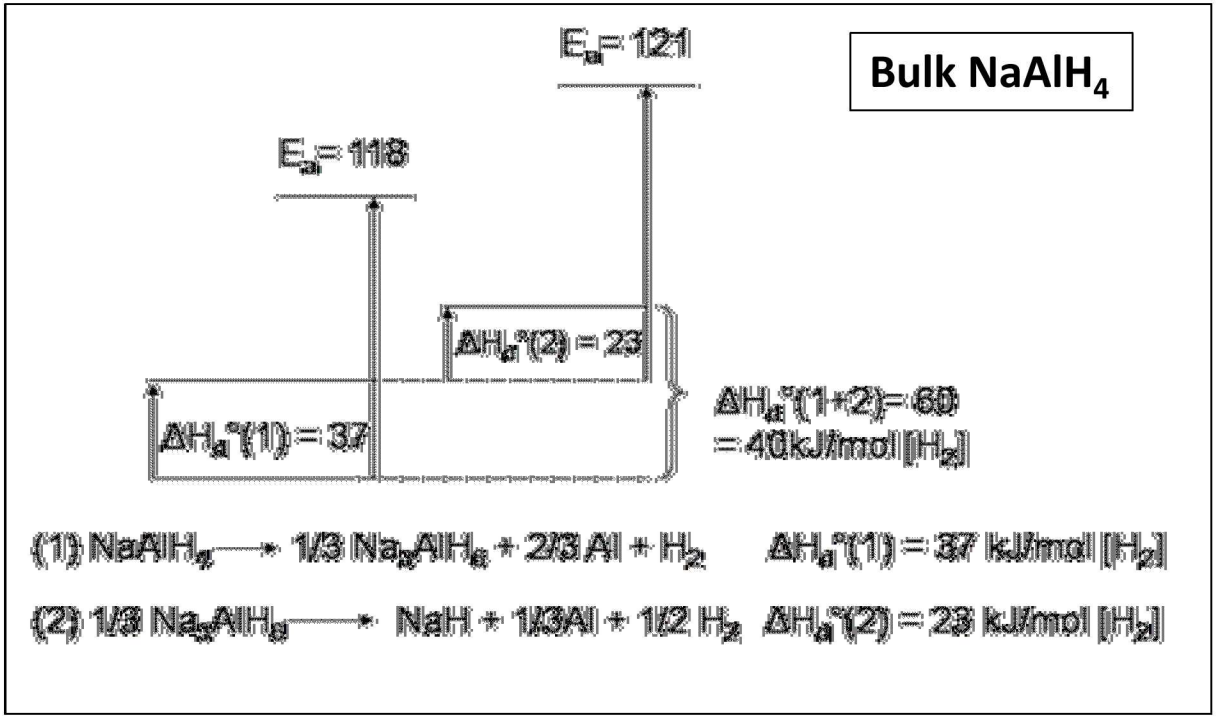
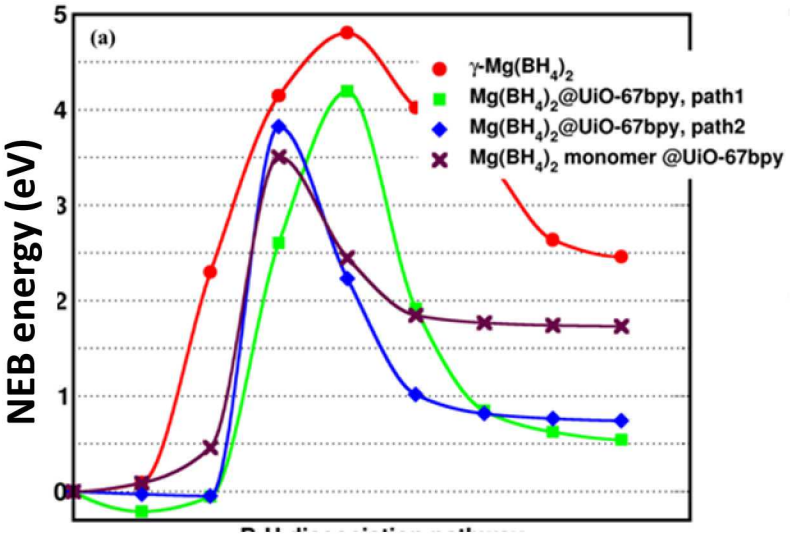
Backup Slides

H_2 release from bulk $NaAlH_4$

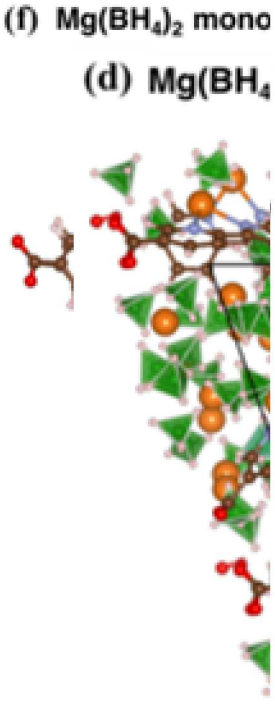


$$NaAlH_4 \xrightleftharpoons[\text{Step 1}]{\text{[Cat.]}} 1/3Na_3AlH_6 + 2/3Al + H_2 \xrightleftharpoons[\text{Step 2}]{\text{[Cat.]}} NaH + Al + 1/2H_2$$

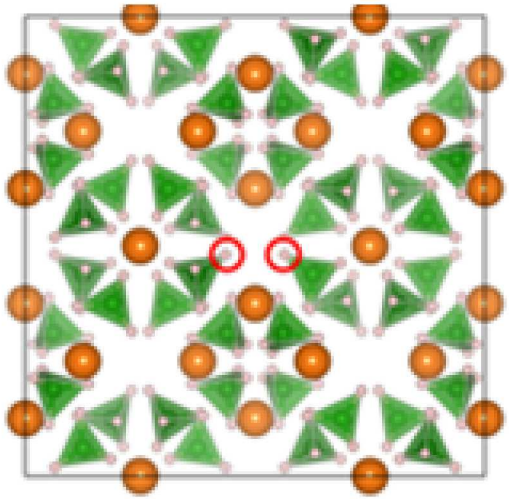
DFT calculations suggest a lower H_2 release energy



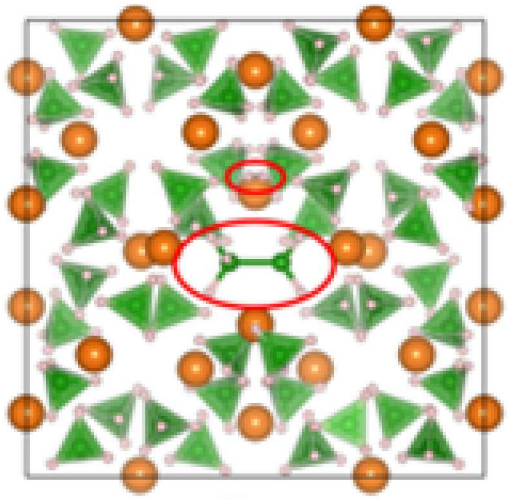
B-H dissociation pathway

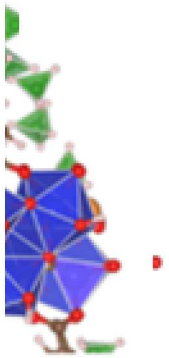


γ-$Mg(BH_4)_2$, initial



γ-$Mg(BH_4)_2$, final



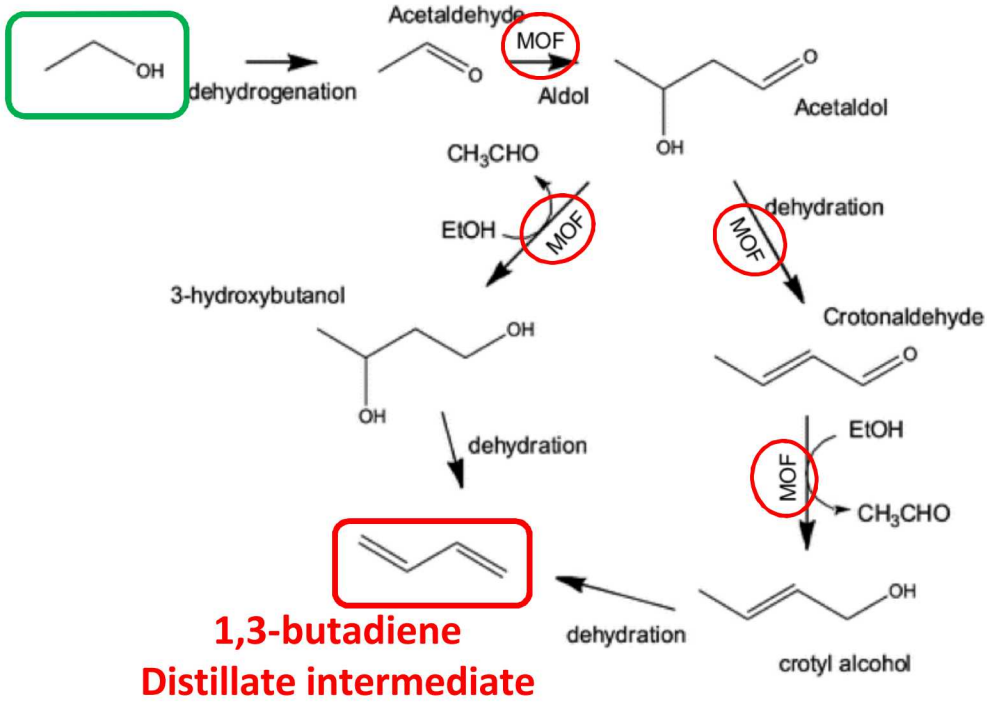


Two binding scenarios:

- **Molecular Dispersion**
- **Molecular Dispersion + formation of small hydride entities inside the pores**

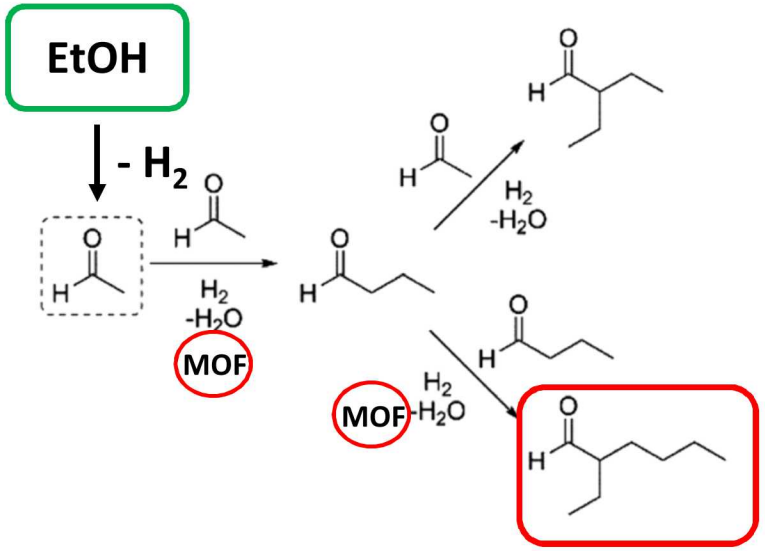
Upgrading ethanol to fuels and valuable chemicals

Butadiene Production (Guerbet Reaction)



1,3-butadiene
Distillate intermediate

2-Ethylhexanal Production (Aldol+hydrogenation)



2-ethylhexanal
Commodity chemical

Alcohols

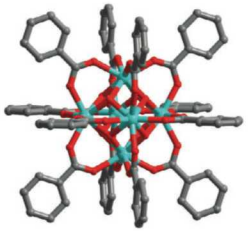
Alkanes

Both targets require C—C bond formation by aldol condensation

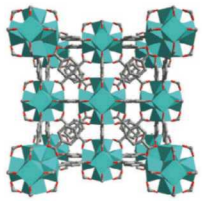
MOFs present a strategy to independently control pore size and density of catalytic sites

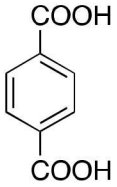
Brønsted acidity is required for catalyzing aldol condensation

Zr_6 nodes in Zr-MOFs are Lewis/Bronsted acidic

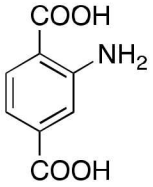


12-connected
7Å and 9Å pores

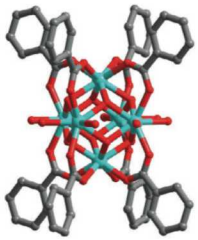




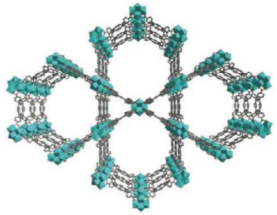
UiO-66

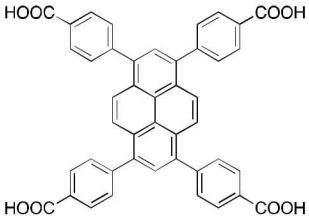


UiO-66-NH_2

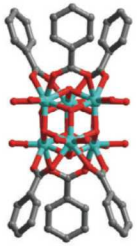


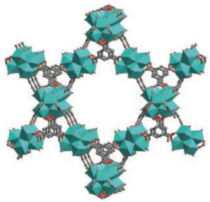
8-connected
30 Å and 15 Å pores



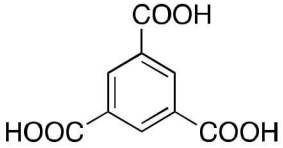


NU-1000





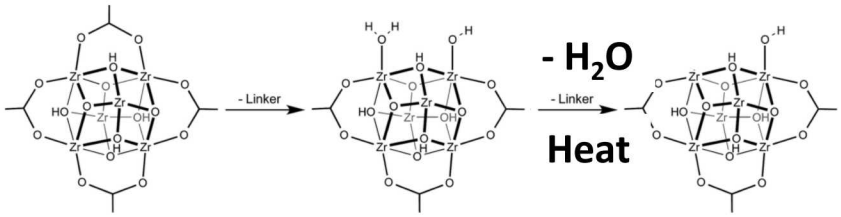
6-connected
17 Å pores



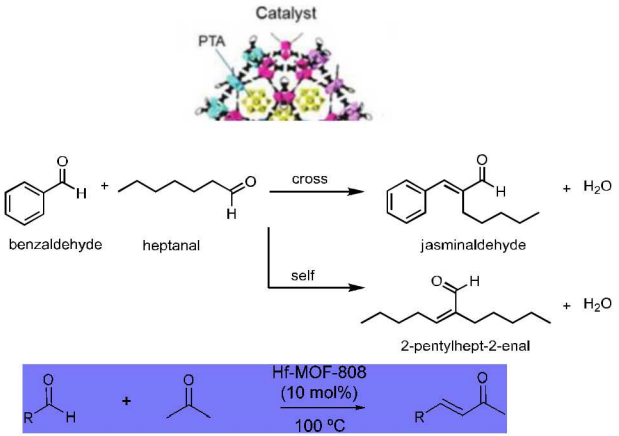
MOF-808(Zr, Hf)

low → **high**

Acidic sites/ Zr_6 node



Several MOFs are known to catalyze aldehyde condensation reactions



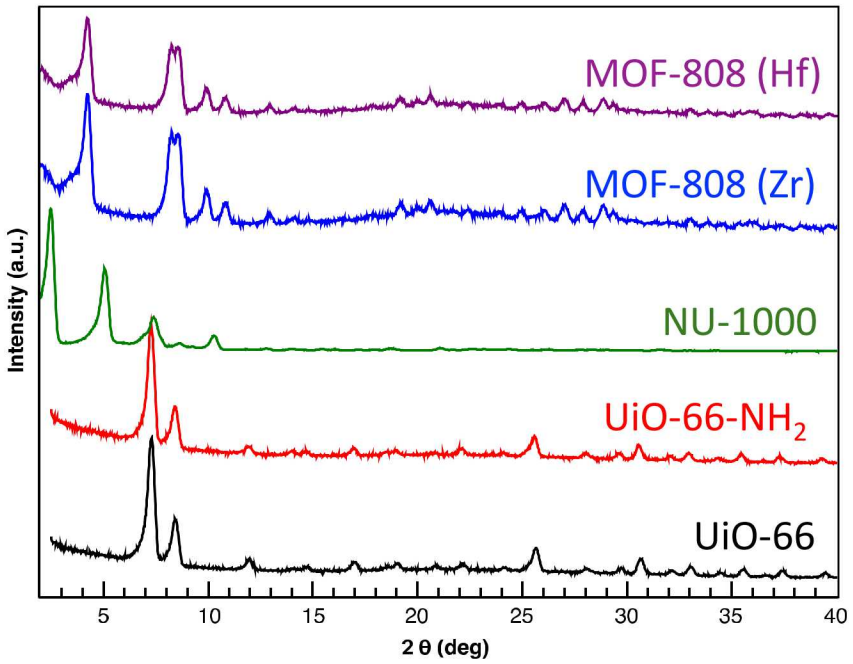
MIL-101 Bromberg & Hatton *ACS Appl. Mater. Interfaces* 2011, 3, 4756

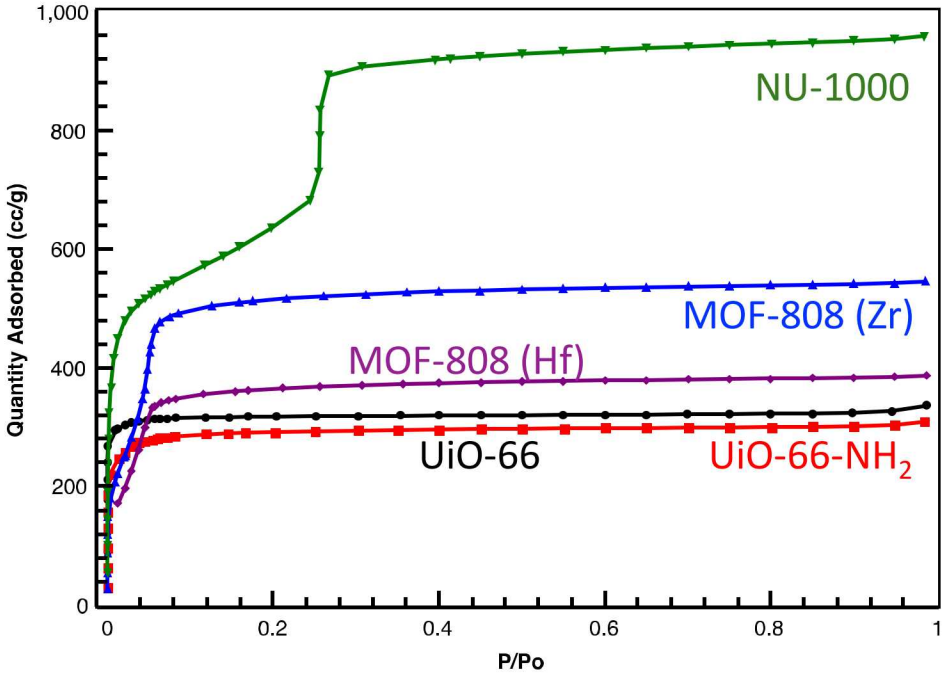
UiO-66(NH_2) Vermoortele et al. *Chem. Comm.* **47** (2011), 1521

UiO-66 and UiO-66(NH_2) Hajek et al. *J. Catal.* **331** (2015), 1

Hf-MOF-808 Rojas-Buzo et al. *Green Chem.* **20** (2018), 3081

MOFs were synthesized following published literature procedures

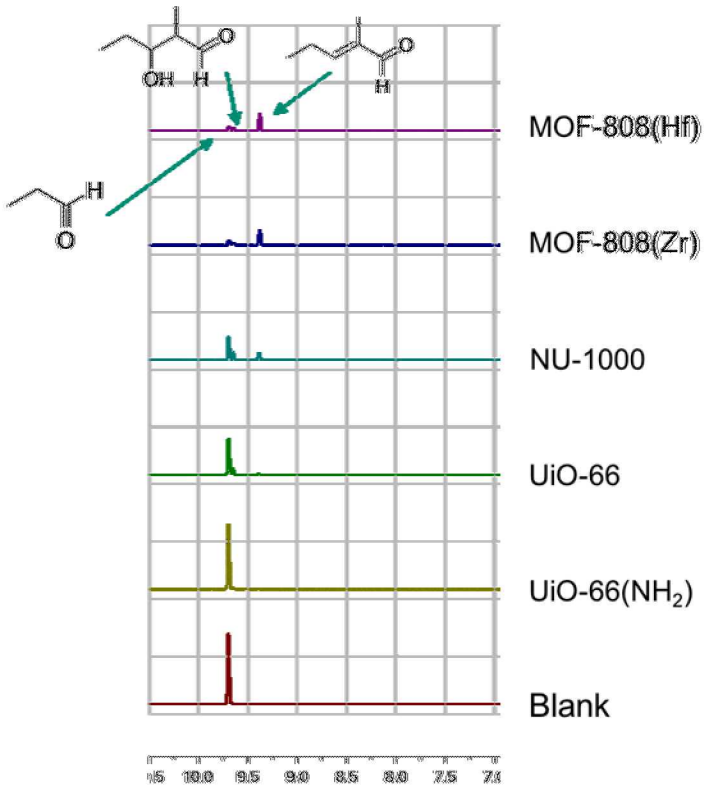




Aldol coupling of aldehydes with MOF catalysts

Goal: Demonstrate control of Bronsted/Lewis acidic sites and pore structure in MOFs to tune the selectivity/conversion of C-C coupling reactions.

Aldol reaction using propanal as model compound



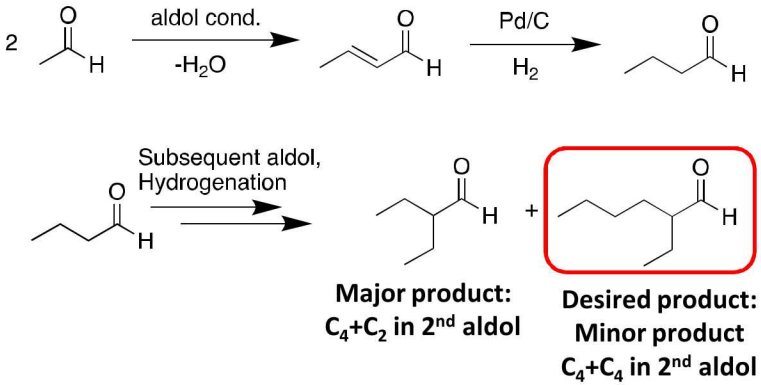
MOF	Propanal Conversion (%)
blank	0
UiO-66 (NH_2)	4
UiO-66	15
NU-1000	36
MOF-808 (Zr)	72
MOF-808 (Hf)	77

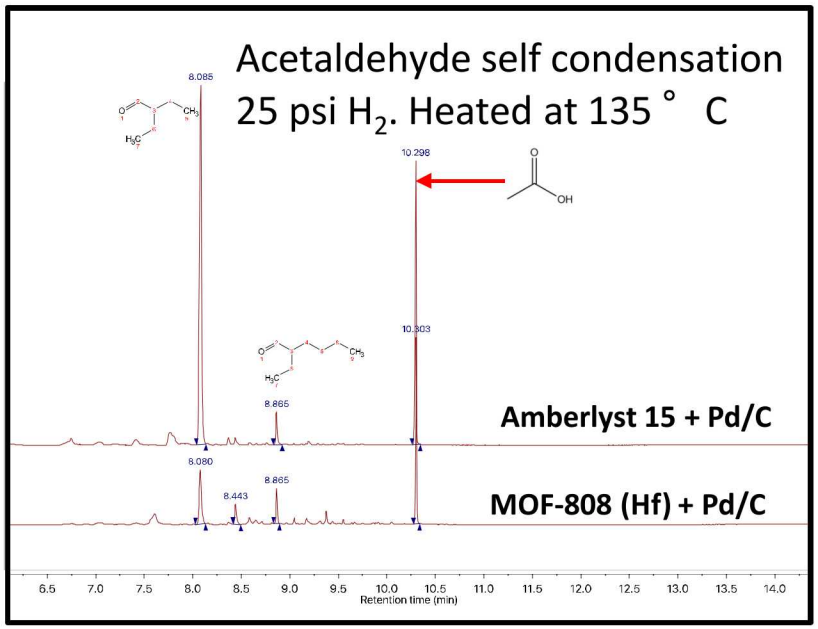
 # acidic sites/node

Result: MOF-808 (Hf, Zr), the MOF [illegible] highest density of (Bronsted+Lewis) acidic sites, shows the highest conversion (77% and 72%) in aldol condensation

Polyaldol condensation reactions under hydrogen to generate high-value C_6 and C_8 products

Goal: increase selectivity for 2-ethylhexanal (2-EH) from < 20% to ≥ 50+% in the cascade reaction





Improved selectivity to 2-EH over commercial catalyst (physical mixture of MOF and Pd/C)

Issues:

- **Selectivity improved but still < 50%**
- **CH_3COOH impurity**

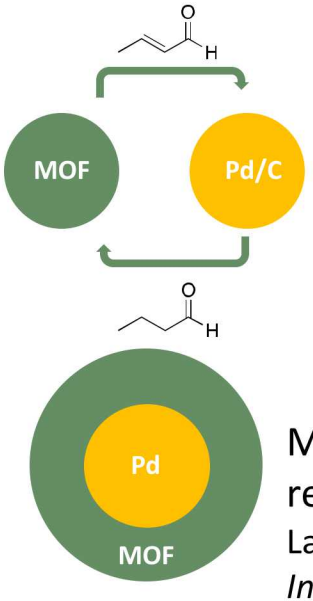
Potential solutions:

→ **Reduce reaction temperature to decrease rate of side reactions**

→ **increase H_2 to create more reducing conditions**

**** In collaboration with Dr. Andy Sutton (LANL)***

Loading with Pd for MPV reduction improves selectivity



Hypothesis: enol diffusion to Pd/C for hydrogenation reduces selectivity

Solution: infiltrate MOF pores w/ Pd

Pd infiltration by $Pd(acac)_2$

Meerwein–Ponndorf–Verley reduction

Larson et al.

Inorg. Chem. **57** (2018), 6825)

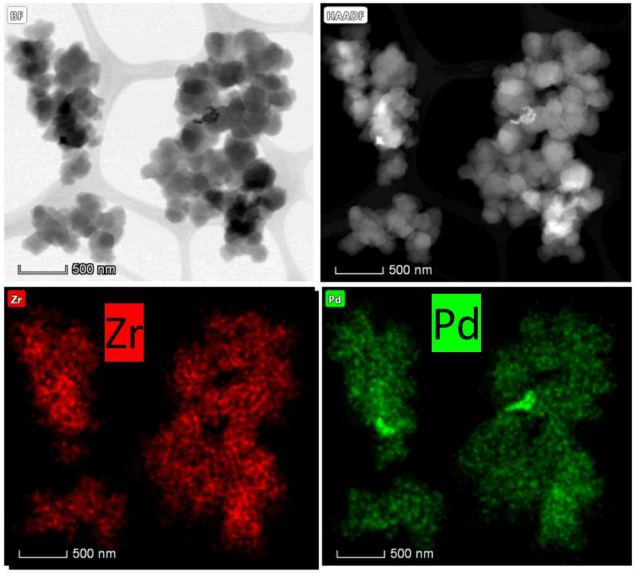
3:1 ethanol:acetaldehyde reaction

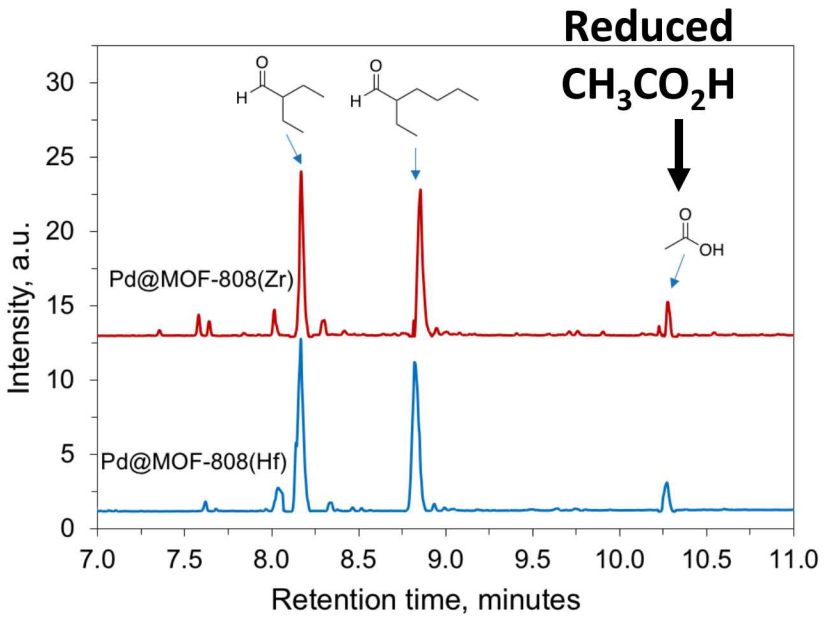
- **MOF-808(M), M=Zr, Hf)**
- **10 bar H_2, 120 C overnight**

Preliminary 2-EH selectivity results:

Pd@MOF-808-Zr	Pd@MOF-808-Hf	Amberlyst 15 + Pd/C (10 wt%)
35%	38%	< 20%

Uniform Pd distribution throughout crystals





Take-home messages

- **Compressed gas (700 bar): physically impossible to meet DOE volumetric target**

→Solid-state materials, including metal hydrides, have potential to meet DOE targets

- **Compressed gas is equally inefficient as a carrier for transporting hydrogen**

→ MOFs can catalyze dehydrogenation of alcohols, which could be low-cost hydrogen carriers

- **Reactions to upgrade biological intermediates (e.g. aryl ethers from lignin) can be catalyzed by MOFs and exhibit higher selectivity than catalysts both homogeneous catalysts and Rainey nickel**